

The production of heavy chemicals from gypsum

Author:

Zahid, Mohammed Saeed

Publication Date:

1957

DOI:

<https://doi.org/10.26190/unsworks/13583>

License:

<https://creativecommons.org/licenses/by-nc-nd/3.0/au/>

Link to license to see what you are allowed to do with this resource.

Downloaded from <http://hdl.handle.net/1959.4/68814> in <https://unsworks.unsw.edu.au> on 2024-04-27

T666.9

7



THE UNIVERSITY OF NEW SOUTH WALES

BOX 1, POST OFFICE, KENSINGTON

26.8.66

ZAHID, Mohammed Saeed

The Production of heavy chemicals from gypsum.

Permission to read and/or photocopy this thesis
has been granted.

Professor
Chem. Eng.

SCHOOL OF CHEMICAL ENGINEERING

THE NEW SOUTH WALES UNIVERSITY OF TECHNOLOGY

"THE PRODUCTION OF HEAVY CHEMICALS
FROM GYPSUM"

by



Mohammad Saeed Zahid.

Submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy in Chemical
Engineering.

N.S

UNIVERSITY OF N.S.W.

27991 26. FEB. 75

LIBRARY

This is to certify that this work was carried out
by the author in the School of Chemical Engineer-
ing, The New South Wales University of Technology.
None of the work has previously been submitted for
a university degree.

A C K N O W L E D G M E N T

The author wishes to thank Professor John Phillip Baxter, O.B.E., Ph.D., A.M.I.Chem.E., F.R.A.C.I., M.I.E.Aust., F.A.A.S., Vice Chancellor and Professor of Chemical Engineering, The New South Wales University of Technology; Chairman, Australian Atomic Energy Commission; and Ex Research Director, General Chemicals Division, Imperial Chemical Industries, for his guidance and interest in the progress of the work.

Thanks are also due to Dr. Eric R. McCartney, Ph.D., for his most valuable assistance and advice throughout the course of this work; to Mr. Frederick W. Ayscough, for the inspection of Australian heavy chemical industry; to the Colombo Plan Authorities in Australia and Pakistan for the opportunity to undertake the foregoing research programme; and to Pakistan Industrial Development Corporation for supplying the samples and geological data of gypsum and coal.

A B S T R A C T.

The aim of this work was to investigate the reactions operative in the manufacture of sulphuric acid and cement from gypsum, silica and a reducing agent such as coal or coke. Small amounts of iron and aluminium oxides usually occur in the raw materials or are added.

A review of the relevant literature is presented and the thermodynamics of the principal possible reactions have been considered. The theoretical background of solid-solid and solid-gas reactions is treated.

The principal method of investigation was to heat various mixtures of the reactants to 1400°C in an electric furnace wound with a platinum-rhodium alloy and to estimate the sulphur dioxide produced after various time intervals. In most experiments, an oxidising atmosphere was maintained; in a few, an atmosphere of nitrogen was used. Several runs were also made at 1100°C .

The rates of reaction of the complete mixture were measured, as well as rates of reaction of simpler

systems made up of one, two or three of the constituents.

Diffusional mechanisms were studied by embedding a crystal of gypsum in carbon, heating, and tracing the penetration of the sulphide layer into the crystal.

The petrological examination of the cement clinker was carried out and the composition of the phases established. A minimum concentration of 90% of tricalcium silicate was found, indicating a very desirable type of clinker. By employing the recommended composition of raw materials 1.3 tons of cement will be obtained per ton of sulphuric acid produced. A description and cost considerations of the proposed plant for the manufacture of sulphuric acid and cement have also been given.

A great deal of effort was directed to evolving and standardizing satisfactory methods for collection and estimation of the products. As a result, a high standard of reproducibility was achieved.

Raw materials from Pakistan, gypsum and coal, from which coke was also prepared, were used to determine whether any new features were introduced.

It was concluded that the Pakistan raw materials were entirely suitable for use in this process. The reaction was found to proceed chiefly through the reduction of calcium sulphate to calcium sulphide and removal of the calcium sulphide by reaction, mainly with additional calcium sulphate. Some calcium sulphide reacted with oxygen. The rate controlling step was the reduction of calcium sulphate by the source of carbon.

I N D E X

Chapter I	Introduction:	Page 1
Chapter II	Literature Survey:	7
	Historical Outline:	7
	Patent Digest:	35
	Important aspects of the decomposition of gypsum: ..	41
Chapter III ...	Thermodynamics of possible reactions:	45
	Thermal decomposition of calcium sulphate:	46
	Thermal decomposition of calcium sulphate in the presence of additives:	48
Chapter IV	Solid-gas and Solid state reactions:	51
	Solid-gas reactions:	51
	Solid state reactions:	53
	Reaction kinetics:	53

EXPERIMENTAL.

Chapter V	Equipment:	60
	Pellet-making press:	60
	Reactor atmospheres:	60
	Reactors:	69
	Studies in the absorption of oxides of sulphur:	100
	Equipment for the estimation of sulphide:	113
	Quenching equipment for cement clinker:	115

Chapter VI	Sources, preparation and analysis of materials:	Page 118
	Sources:	118
	Preparations:	118
	Analysis of coal and coke ash and gypsum:	120
Chapter VII ...	Standardisation of analytical methods and procedure for the run:	141
Chapter VIII ..	Study of solid-solid reactions, clinker and mechanism of reactions:	160
	Study of solid solid reactions:	160
	Study of the cement clinker:	229
	Study of reaction mechanisms:	245

FACTORY LAYOUT and DISCUSSION

Chapter IX	Description and cost consid- erations of the proposed plant for the manufacture of sulphuric acid and cement from gypsum:	320
	Chemical aspects:	320
	Production of sulphuric acid and cement on large scale: ..	321
	Requirements of the raw material and cost consid- erations:	331
Chapter X	Discussion and conclusions: ..	337
BIBLIOGRAPHY:		360

APPENDIX I: .. Analysis of coal and coke
supplied by P.I.D.C.: Page 378

APPENDIX II: . Geological data of coal
and coke: 379

INTRODUCTION.

Pakistan started life as a purely agricultural country. Within a matter of a few years, her economy has undergone a great change. Though basically agricultural, it has become semi-industrial. It has been realised, that in view of the difficulties in ensuring regular supplies of essential raw materials and capital equipment from abroad, industries must be built up round the products of the soil.

The need for the manufacture of heavy chemicals in Pakistan is self explanatory. The object of the present work is to study the manufacture of sulphuric acid and cement from gypsum, which is found in abundance in Pakistan and is a good substitute for scarcely occurring sulfur and sulfide ores.

Gypsum properly defined is the natural mineral form of calcium sulfate dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, formula weight 172.18, sp-gr. 2.31 - 2.33, hardness (Moh's) 1.5 - 2. It is widely and abundantly distributed in nature and occurs in an interesting variety of forms, conditions, associations, and colours. In pure form, gypsum is snow-white and occurs in stratified layers, doubtless of marine origin. Either because of varying conditions at the time of precipitation or through recrystallisation, the mineral occurs in various conditions from hard solid rock to fragmentary and granular forms. In some deposits, the rock occurs in easily friable masses of coarsely crystalline beds, which are appropriately called sugar rock. Many deposits yield the massive mineral through the body of which occur crystals of selenite, these deposits being

described as selenitic gypsum. Most deposits of gypsum occur closely associated with either strata or random occurrences of the mineral anhydrite, suggesting a question of the geological origin and the possible transformation of one form into the other, after deposition. Calcium sulfate occurs in nature as alabaster, selenite, satinspar, anhydrite, gypsite and gypsum sands.

In addition to the salt ranges in West Pakistan where calcium sulfate occurs as gypsum, it is widely distributed over the earth and is commercially available in quantity in most industrial nations. The following table shows the countries, which manufacture sulphuric acid from this source:-

Locality	Date of Installation	Capacity	Raw Material
England:			
Billingham	1929	100,000 tons H_2SO_4 /year under extension to 175000 tons H_2SO_4 /year	Anhydrite
Merseyside	1954	150,000 tons H_2SO_4 /year	Anhydrite
Germany:			
Leverkusen	1916	used as an experimental plant and now dismantled	Initially gypsum, then anhydrite
Wolfen	1938	175,000 tons H_2SO_4 /year	Anhydrite
France:			
Miramas	1937	25000 tons H_2SO_4 /year	Gypsum
Poland:			
Wizow	1950	Unknown	Anhydrite
Buske) Zdroi)	?	Unknown	Gypsum

As far as is known, no special advantage can be claimed for anhydrite or gypsum as sources of calcium sulfate, nor is there any difficulty peculiar to the use of either material. The only known effect is the increased fuel consumption, when gypsum is used because of the heat required for dehydration. The reason why anhydrite is used in certain plants, is its availability in the vicinity. In the present studies, the source of carbon for the reduction of gypsum was a high sulphur coal obtained through the courtesy of the Pakistan Industrial Development Corporation. The problem has been thoroughly examined from theoretical and practical viewpoints by studying systems composed of pure as well as naturally occurring raw materials.

The possibility of obtaining SO_2 from gypsum, by heating it with clay in a shaft kiln was first suggested in 1903 by Lunge. During the first world war, the Germans used coke to reduce calcium sulphate in two rotary kilns at Leverkusen, but no attempt was made to prepare cement from the clinker. In late twenties at Billingham, England, ammonium sulfate was produced from anhydrite. Afterwards technical and cost studies showed the production of sulphuric acid with cement to be more economical from anhydrite by reacting with acidic oxides and a reducing agent.

The main points to be noted as summarised by A. Fleck(50) are:-

- (a) The kiln section of the process, to be economic, must be carried out in large units of not less than the equivalent of 40,000 tons SO_3 per annum.

- (b) The control of the reactants must be kept to very close limits.
- (c) The capital required for the process is large, being in the ratio of 1 : 2 : 4 for a ton-year of product for H_2SO_4 , from elemental sulfur from pyrites and from anhydrite respectively.
- (d) The reaction has hitherto only been successful when carried out in a large rotary kiln of the cement type. The new kilns now being installed are 365 feet in length and ten feet in average diameter.
- (e) The operating cost per ton of product, making due allowance for the whole capital required, should come slightly below the operating cost of H_2SO_4 from pyrites.

This is a generalised statement that may not be true in all circumstances.

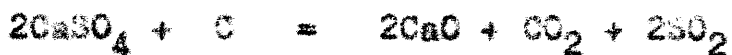
Chemical aspects of the anhydrite process:-

There are three chemical aspects of the anhydrite process.

- (a) Liberation of SO_2 in rotary kiln:-



The above 3 stages can be summarised in the following equation



This equation is over simplified and the importance of reaction 3 is to be kept in view.

- (b) Cement clinker is produced in the kiln by the reduction of calcium sulfate with coke and subsequent reactions with acidic oxides, supplied in the form of clay or ashes. The composition of raw materials is strictly controlled.
- (c) The kiln atmosphere should be oxidising. The exit end especially must be maintained on the oxidising side, which avoids the contamination of clinker with sulfides and elemental sulfur.

The limitations of the process are the large size of the installation and the cost per ton/year of the sulfuric acid to be produced. To overcome this it has been suggested to heat the raw materials in closed retorts, by the application of external heat, eliminating the use of oxidising air and converting concentrated SO_2 so obtained to sulfuric acid in conventional plants of 5000 tons capacity/year.

The present work deals with the decomposition studies in both oxidising and non-oxidising atmospheres. Production of maximum amount of sulfuric acid and a good quality cement has been the main target. Subsidiary reactions have also been studied to investigate the mechanisms involved.

CHAPTER II.

LITERATURE SURVEY.

(According to the recommendation of the report of the Committee for the reform of inorganic chemical nomenclature (Journal of the Chemical Society 1940 pp. 1404 - 1415). The chemical elements and their compounds have been represented extensively by their formulae.)

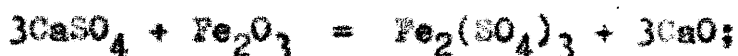
CHAPTER II.

LITERATURE SURVEY.

I. Historical Outline:-

As early as 1907, in a French patent (7) on the extraction of sulphur from gypsum, there is a mention of reduction with the products of distillation from waste carbonaceous substances, the CaS obtained being decomposed with H_2CO_3 into H_2S and CaCO_3 . Hofman and Mostowitsch (64) in 1908, studied the behaviour of CaSO_4 at elevated temperatures. The CaSO_4 as well as the fluxes, silica, ferric oxide, and lead monoxide were prepared with great care to secure purity. By heating CaSO_4 alone in an electrical resistance furnace it is found that no change except loss of moisture takes place up to 1150° . At 1200° decomposition sets in, which becomes complete at 1360° , accompanied by partial fusion. Silica lowers the temperature of complete decomposition to about that at which it begins in pure CaSO_4 . With Fe_2O_3 , decomposition of CaSO_4 sets in at 1100° and is strongest at $1200 - 1250^\circ$. At 1250° the charge of Fe_2O_3 and CaSO_4 melts completely to a ruby red liquid consisting of calcium ferrite containing CaO and CaSO_4 in solution. PbO has no effect upon the decomposition of CaSO_4 , since it begins to volatilise at 700° . The advantages and disadvantages of these fluxes are discussed with reference to a number of metallurgical processes. The general guiding principles are that, in a roasting process, where free excess of oxygen is desirable, fusion is to be avoided and therefore the presence of Fe_2O_3 , whereas the decomposition of CaSO_4 , being a strongly

endothermic reaction (-95, 600 cal) tends to prevent local fusion. For a fluxing process low melting combinations are usually desirable. The fact that a basic dolomite furnace lining is less rapidly attacked by an acid silica flux than by a basic one containing Fe_2O_3 is explained by the ready fusibility of calcium ferrite. Auzies (8) in 1910, described the manufacture of sulphuric acid by calcining a mixture of CaSO_4 (anhydrous) and Fe_2O_3 , the action being



and on heating to or above the temperature of dissociation.



The gaseous products are led over MnO_2 or Mn_2O_3 or over WO_2 or W_2O_3 or over Mo_2O_3 or ThO_2 at 200° .

Frey (53) mentions that the view generally obtains that raw materials containing S for the manufacture of H_2SO_4 , other than pyrites, cannot successfully compete with the latter. But in countries remote from supplies of pyrites and having their own supply of CaSO_4 , the possibility of successfully using the latter as raw material appears not altogether hopeless. The results of a series of calcining experiments with various mixtures of crude CaSO_4 and SiO_2 or sand are given. The CaSO_4 is decomposed within a short time under the conditions of the experiments. Presence of small amounts of Fe_2O_3 favours decomposition but addition of $\frac{1}{4}\text{ Fe}_2\text{O}_3$ does not seem to accelerate the reaction velocity beyond a certain point.

Wedekind and Co. (128) employed a process whereby

the decomposition of gypsum by means of sand can be effected by roasting the mixture of the crude materials with so much pyrites that the heat liberated by roasting the latter is sufficient for the decomposition of the gypsum by means of SiO_2 . The process is applicable in the treatment of the gypsum slimes obtained in the manufacture of H_2SO_4 .

In 1911 Hofman and Kostowitch (65) found that CaSO_4 is reduced by C and CO without loss of water. The reduction by CO begins at 700° and is finished at 900°C . The reduction by C in a neutral atmosphere begins at 700° and can be considered finished at 1000° . Roasting CaS in pure dry air forms a product of 76% CaSO_4 or 26% CaO , with a loss of 32% S. This interaction takes place in a neutral as well as in an oxidising, but not in a reducing atmosphere.

In 1920, Kasselitz (70) described a process developed in Germany during the war to produce S required for H_2SO_4 and H_2SO_3 manufacture, which consisted in reducing gypsum with coke and converting the resultant SO_2 into trioxide by a contact process. Cement is manufactured from the byproducts. For the production of sulfur gypsum is heated with coke or coal in a rotary furnace to 1100° and the CaS is treated with steam to form H_2S which is finally oxidised in a contact furnace. The purity of the product is 99.95%.

Dominik (44) in 1921 worked on the problem of the production of sulphuric acid from gypsum. According to him, gypsum may be converted into $(\text{NH}_4)_2\text{SO}_4$ and the latter into NaHSO_4 , from which free H_2SO_4 may be obtained by (a) reduction of the free acid to SO_2 and re-oxidation, (b) distillation with ballast (c.f. C.A. 15.2155) (c) crystall-

isation of hydrated Na_2SO_4 by cooling and concentration of the mother liquor. Na_2SO_4 increases in solubility with addition of free H_2SO_4 to a maximum, above which the acid sulfate separates. The solubility also decreases rapidly with the temperature; at -11° , the maximum solubility corresponding to 32% free acid is only about 4% Na_2SO_4 by weight, so that at this temperature, a fairly complete separation can be obtained in one operation. A calculation of the water required and fuel consumption necessary for the decomposition of the acid salt at a given temperature is added.

Zawadzki, Kossak and Harbut (137) in the same year published their work on the reduction of CaSO_4 and MgSO_4 . At temperatures, below 900° , CaSO_4 is reduced to CaS by C, the reaction is quantitative about 900° , the velocity of reaction is sufficient for technical purposes. The CaS yields H_2S quantitatively, on heating with MgCl_2 solution. Above 900° CaO and SO_2 are also produced in quantities increasing with rise of temperature. MgSO_4 on reduction with CO is almost completely converted into $\text{MgO} \cdot \text{SO}_2$ and free S. MgSO_4 reduced with H_2S above 700° yields MgO , while CaSO_4 under similar conditions is converted into CaS . The products of the reduction of CaSO_4 and MgSO_4 by carbon are dependent on the temperature and the ratio of carbon to sulphate; at lower temperatures and with excess of carbon, MgSO_4 leaves a residue containing MgS as well as MgO , in the case of CaSO_4 , the residue is sulfide only. At higher temperatures and with less carbon the products are MgO , CO_2 and S and CaO and SO_2 respectively.

In 1923 Budnikoff and Syrkis (34) published their

work on the dissociation of CaSO_4 at high temperatures. According to them, the dissociation of CaSO_4 is very small up to 1000°C , equilibrium occurring with 0.21% of free CaO at that temperature. At 1300°C 3.0% CaO is present and the mass begins to melt, evolving copious fumes. At 1375°C dissociation is practically complete, only 1.33% of CaSO_4 remaining undecomposed.

Another paper in the same year by Wöhler, Martin and Schmidt (132) describes the formation of sulphur by the action of SO_2 on the sulphides of calcium, zinc and iron. SO_2 acts on CaS at temperatures below 1000° to give the sulphate and S , but this reaction is soon brought to a standstill owing to the formation of a protective layer of sulphate on the pieces of sulphide. By working at temperatures above 1000° , this can be avoided, as the reaction products are lime and S . The low temperature reaction can however be accelerated by the addition of triferrous tetroxide, which acts as a catalyst. Zinc blend reacts with SO_2 to give the oxide and S , but here again the reaction velocity rapidly diminishes owing to the formation of a protective layer, in this case of basic sulphide. Both sulphides of iron react with SO_2 to give triferrous tetroxide and S . The reaction is rapid and complete, being catalytically accelerated by the oxide.

Another paper by Marchal (78) on the action of silica and alumina on CaSO_4 , appeared in the same year. Using a method similar to that employed previously (cf. A. 1323.ii, 139) viz the dissociating of silver sulphate (79), the author has studied the reactions





by measuring the equilibrium pressures at different temperatures (the systems being univariant). The first reaction begins at 870° , the second at $940 - 950^\circ$, both being studied up to 1280° . Both are very rapid; thus if gas is removed at 1238° , equilibrium is restored in a few seconds. For the first reaction, the total gas pressure becomes 760 mm at 1273, for the second at 1363° (extrapolation value). The difference between these two temperatures is in keeping with the difference between the heats of formations of calcium silicate and calcium aluminate.

Again in the same year Hutin (67) published a paper on the production of sulphuric acid from gypsum. Several methods for recovery of sulphur are mentioned briefly e.g.

- (i) Helbig and Schaffner's treatment of waste black ash from the Leblanc process with HgCl_2 to form CaCl_2 , H_2S and HgO , the cycle



- (ii) Feld's polythionate process, by means of which Germany replaced the importation of 300,000 tons pyrites per year.

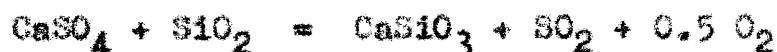
- (iii) and finally the process, developed by the Badische Co., in which CO_2 and NH_3 are bubbled, under pressure, through a hot slurry of CaSO_4 in H_2O to form CaCO_3 and ammonium sulphate.

Molitor (92) in 1924 published his work on producing sulphuric acid and sulphates from natural gypsum. The Barmasch process (C.A.9,1233,2804;10,95;17,3578) based on the work of Hofman and Mostowitch (C.A. 3,2415) and the principle of flameless surface combustion are described from the manufacturing point of view. Related processes, e.g. of Basset (C.A.3,749;7,3653;10,814,2977), Auzies (C.A.5,914;6,1968) and the "Badische" (C.A.17,3578) are included.

In 1925 Marchal (80) published another paper on the thermal dissociation of metallic sulphates. According to her, anhydrous calcium sulphate affords evidence of dissociation at 960° and the dissociation pressure reaches 9.7 cm at 1230° . For a mixture of equal moles of anhydrous calcium sulphate and amorphous silica the dissociation becomes evident at 870° and the dissociation pressure reaches 81.7 cm at 1280° . The partial pressure of sulphuric anhydride at equilibrium is given by the equation

$$\log p_{\text{SO}_2} = -17818/T - 11.87 \log T + 49.27$$

whence the heat of the reaction



is calculated to be 74.6 cal at 15° , whilst that determined from thermochemical values is 76.6 cal. The dissociation pressure curves when quartz or amorphous silica is used are not sufficiently different to determine the heat of crystallisation of silica. When gas is removed, the system becomes polyvariant, due probably to dissolution of one of the solid phases in the other. Corresponding mixture of alumina with CaSO_4 afford evidence of dissociation at 950° . The dissociation pressure reaches 16.7 cm at 1270° and the total

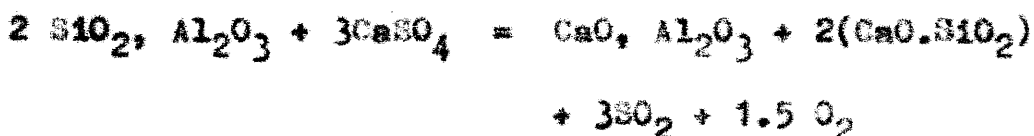
pressure at equilibrium is given by the expression

$$\log P = 76814/T + 136.7 \log T - 484.4$$

By analogy with the results from silica mixtures the reaction may be represented by the equation.



The reaction between anhydrous calcium sulphate and anhydrous kaolin is assumed to take place according to the equation



The reaction is univariant so long as no gas is removed. Different kaolins give different results. Generally the reaction becomes evident at 780° and the dissociation pressure attains 100 cm at about 1160° . The reaction of the CaSO_4 with Fe_2O_3 is complicated by the inner equilibria of the Fe_2O_3 . It is assumed to follow the course



and is practically univariant, so long as no gas is removed. The reaction is evident at about 1000° , and the dissociation pressure attains 27.3 cm at 1280° . Chromic oxide does not react with CaSO_4 . The bearing of the results on the recovery of H_2SO_4 , in the Carmichael-Bradford process of lead smelting, and from gypsum is discussed. She also calculated the heat of dissociation of CaSO_4 (8/).

Budnikoff (33) in 1925 studied the action of gaseous substances on gypsum at high temperatures. He records the action of gaseous substances on gypsum at high temperatures about 1000°C . Air at 1000° gives traces of SO_3 . The reaction



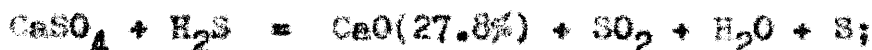
is almost complete at 920° , at higher temperatures SO_2 is formed:



Dry hydrogen at 1000° causes a 70% conversion of gypsum into CaS , but steam at the same temperature produces only slight decomposition, unless charcoal is present. With hydrogen sulphide at 1000° the reactions:



and



occur.

In 1926 Müller (95,96) published an account of the gypsum-sulphuric acid process as employed by F. Bayer & Co. Calcium sulphate in the form of gypsum or anhydrite is reduced by carbon in the form of coke at 800° according to the equation



The lime must be recovered in a marketable form to make the process economically possible, and clay is therefore added to the raw materials in the requisite proportions to obtain Portland cement. The operation is carried out in a

rotary kiln fired with pulverised fuel. The materials must be dried before entering the kiln in order to obtain a sufficiently high concentration of SO_2 in the issuing gases. An oxidising atmosphere must be maintained in the kiln to prevent the formation of carbon oxysulphide in the gases and calcium sulphide in the cement clinker. In practice, about half the theoretical quantity of coke is used to prevent too rapid reduction and the formation of CaS in the clinker.

Marchal (82), studied the action of silica upon metallic sulphates. At high temperature, SiO_2 displaces SO_3 from sulfates of Ca , Ba , and Mg because of the latter's volatility, although the reactions are extremely endothermic (-99.2-Cal for CaSO_4 , -122.3-Cal for Ba SO_4). At the temperatures employed SO_3 is largely dissociated into SO_2 + $\frac{1}{2}\text{O}_2$. Gradual cooling in contact with the paper regenerated the sulphate, so that the equilibrium pressures could be measured by the static method. These pressures were considerably higher than the decomposition pressures of the sulfates alone (cf. CA. 20.346). The dry sulfates and SiO_2 were powdered together extremely finely. The temperature at which the pressures reached 10 m.m., when heated alone and with silica were respectively for CaSO_4 1235° , 1105° ; BaSO_4 about 1800° , 1255° ; MgSO_4 1030° , 675° . The practical application in obtaining H_2SO_4 and Ca SiO_3 for cement clinker from gypsum is suggested.

A review of the recovery of SO_2 from gypsum by Neumann (79) appeared in the same year. The patent literature on the subject is thoroughly reviewed in it, with

comments on many processes. However, he leaves out of consideration all processes that aim at producing some commercial sulphate like ammonium sulphate or at bringing about the decomposition of CaSO_4 by heat alone, a reaction occurring at too high a temperature (1375°) for economic success. Such processes as the Bernburg-Halbeck (roasting with coal to CaS from which H_2S is liberated by HgCl_2 and the H_2S converted to S in Claus furnaces), the treatment of CaSO_4 coal mixtures in shaft furnaces; of $\text{CaSO}_4 + \text{H}_2\text{O}$ gas, in shaft furnaces, or treatment of CaSO_4 with coke in a revolving grate generator (Duisburg) have not been successful in peace times. The gypsum - SO_2 process in which slag sand cement is made as a by-product has, however, survived. In this process, anhydrite or gypsum is finely ground with shale and coke and burned to clinker in a rotary kiln. The clinker is then ground with slag sand. To reduce the temperature at which CaSO_4 decomposes or to give at the same time a second product of value, processes have been suggested in which the following additions to CaSO_4 have been made: Quartz, clay, coal, clay + Coal, pyrite's, and other metallic sulfides, sand and pyrite's, sand + alkali sulfate. Several of these substances lower the temperature at which SO_2 is given off; especially is this true of kaolin. Much space is given to experiments on the liberation of SO_2 by the reaction

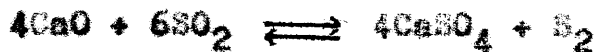


Frydlander (54) also describes in his paper, Badische, Otto, Bayer and Bassett processes. In Otto process, the reaction of the Badische process is carried out in a special

tower. He has also given a comparison of the Bayer and Bassett processes. Similarly Teytovitch (122) describes the process of the production of sulfuric acid from gypsum as used by Germany during the war and Molitor (73) discusses the chemistry and engineering of various processes.

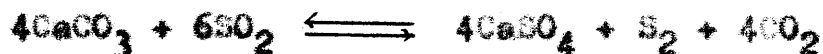
Losev and Nikiten (74) in 1929 published their work on the pyrogenic decomposition of gypsum. In their estimation the so-called fusion of gypsum is an optical illusion. Decomposition is noticeable above 1000° and maximal at 1420° , the decomposition temperature may be lowered by addition of silica, alumina or ferric oxide. Reduction by charcoal is best effected at 1000° .

Equilibrium studies concerning the system Ca-S-oxygen were done by Schenck and Jordan (109). According to them Birnbaum and Wittich (24) found indications that at 500° , $4 \text{ CaO} + 4 \text{ SO}_2 \rightleftharpoons 3 \text{ CaSO}_4 + \text{CaS}$ (a) takes place. Schenck and Jordan have found that at 600° , CaO and SO_2 do not unite mol for mol. Since a deposit of sulfur was observed, according to the equation



Sestini reported (113) $\text{CaSO}_4 + \text{S}_2 \rightleftharpoons \text{CaS} + 2\text{SO}_2$ (b). It is concluded therefore, that the reaction of CaO and SO_2 takes place in two steps, i.e. a and b. An attempt was made to determine the equilibrium pressure at the univariant point and to explain and evaluate the equations on the basis of the phase rule and the mass action equation. It is suggested that the presence in nature of sulfur deposits

together with gypsum in the neighbourhood of calcium carbonate may be explained by



Parrish (101) in his article on the significance of the production of H_2SO_4 from anhydrite mentions the introduction of this process, worked out at Leverkusen, at Billingham. A discussion of the reactions involved between coal anhydrite and clay or shale, giving cement and H_2SO_4 and an account of different steps in the process are given. Cost analysis shows that the price of spent oxide will not be affected adversely by this competing process.

In 1930, Adadurov, Deribas and Kraini (3) worked on the dissociation of gypsum in presence of catalysts. By proper choice of catalysts the yield of SO_3 at 600° can be raised from 0.18 to 25.85%, whilst that of SO_2 is reduced to 0.54% (with MnO_2 as catalyst). Numerous catalysts were employed. The results are in accord with the resonance theory of catalysts.

In the same year a few papers appeared on cement produced in the process. Mullan (94) studied the effect of gypsum on the decomposition of tricalcium silicate by heat and found that the liberation of CaO from $3\text{CaO}.\text{SiO}_2$ by heating at 1000° is accelerated by the addition of gypsum. It may prove possible to use this phenomenon as a measure of the quantity of $3\text{CaO}.\text{SiO}_2$ in cement.

Caddick's article (38) deals with the economics of

the anhydrite process. CaSO_4 as a source of H_2SO_4 has been dealt with along two main lines (1) The recovery of S in the elemental form and (2) obtaining the S in the form of SO_2 . Brief outlines of these processes are given, as well as the reactions in the production of SO_2 in conjunction with Portland cement manufacture. For the latter process the residues from the reduction, powdered shale, clay, sand etc. are intimately mixed with the CaSO_4 . Comparative costs of materials and of plant and manufacture are given, showing that anhydrite can only be considered as a source of S for H_2SO_4 manufacture, when joint manufacture of cement is undertaken and even then the margin is such that local conditions as to pyrites or other sources of S would have a direct bearing as to its economic value.

Zelinski and Rakuzin (138) discuss briefly two simplified methods for the manufacture of H_2SO_4 from gypsum. The first consists in heating a mixture of anhydrous CaSO_4 , coal, sand and clay in the presence of a catalyst (Fe_2O_3). The resulting gases SO_2 , CO_2 and O_2 are suitable for chamber and contact processes. The resulting solid by-product is Portland cement. The second method consists in mixing 4-in. lumps of anhydrous CaSO_4 with coke in the proportion 4 : 1 and burning the mixture in a rotary generator, into which compressed air is blown



The solid by-product is treated with water and may be used as fertiliser.

Zawadski and Syryczynski (134) studied the reversibility

of the reactions between SO_2 and lime and between CaS and CaSO_4 . The equilibrium in $\text{CaS} + 3\text{CaSO}_4 \rightleftharpoons 4\text{CaO} + 4\text{SO}_2 + 238.6 \text{ K. cal.}$ was studied from both directions. The equilibrium pressures of SO_2 were found identical in all cases, although, according to the secondary reaction $\text{CaS} + 2\text{SO}_2 \rightleftharpoons \text{CaSO}_4 + \text{S}_2 + 58.9 \text{ K.cal.}$ (b), the composition of the solid phase of the system (a) was altered. The pressures of SO_2 in contact with CaO at the beginning of the saturation by passage of the gas across a solid layer are a little smaller than those of the equilibrium, whereas the pressures of the same gas at the beginning of the decomposition of $\text{CaS} + 3\text{CaSO}_4$ exceed those of the final equilibrium. The results seem to exclude the possibility of explaining these anomalies by admitting the formation of solid solutions and intermediate compounds. The abbreviated Nernst equation was used for calculating the thermic effects. The heat of reaction (a) was found to be 232.4 to -5.5 Cal., av. 234.1 Cal; that of reaction (b) 61.1 - 57.2 Cal.

Terres (118) in 1931 wrote an article on gypsum as the raw material of Chemical Industry, in which he describes three types of processes, which commencing from gypsum lead to the useful recovery of S or SO_2 . In the first $(\text{NH}_4)_2 \text{SO}_4$ is prepared by double decomposition and then heated with Na_2SO_4 . The NaHSO_4 produced on further heating evolves SO_3 . The second method is the thermal decomposition of gypsum or Kieserite. The latter is completely dissociated at 1150° , but the presence of Cl and HCl in the gases causes difficulty in their utilisation for H_2SO_4 making. The decomposition of gypsum only begins at 1200° , and is therefore necessary to add SiO_2 , Al_2O_3 or Fe_2O_3 . The

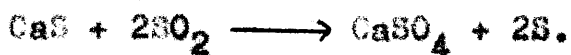
influences of the three decreases in the order mentioned. A series of dissociation pressure curves for mixtures of gypsum with each is given. This process is still worked at Leverkusen, yielding saleable cement as a by-product. Another process of this type consists in the treatment of gypsum or mixtures containing it with coke in a blast furnace, the product being sulphur. The third group of processes consists in the reduction of gypsum to sulphide by roasting with coke or coal in a rotary kiln. Further treatment may consist in decomposition with CO_2 and recovery of S by the Chance-Claus process. Or the CaS may be decomposed with superheated steam in a shaft furnace: $\text{CaS} + \text{H}_2\text{O} \rightleftharpoons \text{CaO} + \text{H}_2\text{S}$. This reaction commences at 1000° and with rise in temperature the equilibrium moves to the right; SO_2 is also formed by subsidiary reactions. These are very complex and as they occur under the conditions present in a gas producer, they explain the occasional presence of free S in producer clinker.

Weyer in 1931 (130) studied the formation of clinker compounds under practical kiln conditions at about 1300°C .

In 1932, Adadurov and Pligunov (2) published a paper on the dissociation of gypsum in presence of catalysts up to 1200° . According to them displacement of SO_3 by SiO_2 is not a chemical but a catalytic reaction, contrary to the opinion of Terres, the addition of Al_2O_3 , Fe_2O_3 and Cr_2O_3 is similar to that of silica, the quantity having little effect on the yield of SO_3 . Cr_2O_3 was best, giving 100% decomposition in one hour. Adadurov (4) also stated that since the heat of activation at $700 - 900^\circ$ is only

9500 g.cal. per mol, the decomposition must depend on intra molecular re-arrangements. At $900 - 1100^{\circ}$ the process is catalytic. Again Adadurov, Galameeva and Gernet (4) studied the thermal dissociation of chemically pure gypsum in presence of oxides of iron, Aluminium, and Chromium. The heat of reaction is 6000 - 9000 g-cal at $900 - 1000^{\circ}$ and 35000 - 48000 g-cal at $1000^{\circ} - 1200^{\circ}$. SiO_2 , Fe_2O_3 and Cr_2O_3 greatly increase the yield of SO_2 or SO_3 even at less than 900° . The heat of activation at 1000° to 1200° is $\text{CaSO}_4 - 99000$; $\text{CaSO}_4 + \text{SiO}_2 - 27000$; $\text{CaSO}_4 + 5\% \text{Al}_2\text{O}_3 - 48000$; $\text{CaSO}_4 + 3\% \text{Fe}_2\text{O}_3 - 32000$; $\text{CaSO}_4 + 3\% \text{Cr}_2\text{O}_3 - 40000$ g.cal. Mixed catalysts are not additive in their action. $\text{SiO}_2 + \text{Fe}_2\text{O}_3$ and $\text{SiO}_2 + \text{Al}_2\text{O}_3$ mixtures are more and $\text{SiO}_2 + \text{Cr}_2\text{O}_3$ mixtures less efficient than calculated on additivity basis, showing the dissociation is a catalytic process.

Volkovich (124) in the same year published an account of the utilisation of gypsum for the manufacture of H_2SO_4 and cement, while Trifonov (121) gave a new explanation for the easy decomposition of CaSO_4 in blast smelting galena by the Carnichael-Bradford method. According to this explanation there is a partial reduction of gypsum to CaS which sets in at about 500° . Above 850° , the CaS reacts with CaSO_4 to form CaO and SO_2 , but the complete decomposition of the gypsum in this manner is hindered by the reaction



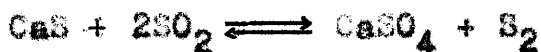
Only above 1000° can lime completely free from SO_4 be obtained; for above this temperature, the reaction



Zawadzki (133) in his studies of Ca-S-oxygen system, determined the equilibrium pressures in the system $\text{CaSO}_4 \rightleftharpoons \text{CaO} + \text{SO}_2 + 0.5 \text{O}_2$ over the range $840^\circ - 1373^\circ$, equilibrium was approached from both directions. Over 1000° , dehydrated gypsum changes to anhydrite. The first form of anhydrite may alter to another at 1200° . In the systems



and



good agreement with prior thermodynamic data was obtained.

Budnikov and Nekrich (35) in their article on the manufacture of Portland cement from anhydrite and gypsum recount the difficulties which arise. The temperature best suited for decomposition of CaSO_4 is close to its melting point; the $\text{CaSO}_4 \cdot \text{CaO}$ which is formed during decomposition also has a low m.p and COS is formed in the reducing atmosphere. In their opinion, experiments on commercial scale alone can determine the practicability of the process.

Rojak, Gerschman and their colleagues (106,107) conducted experiments on the preparation of SO_2 and Portland cement from gypsum. They took a 2 : 0.37 : 0.1 mixture of gypsum, clay (containing 20% H_2O) and C, which yields on firing at 1450° Portland cement (SO_3 content \times 1.9%), the reaction gases are free from H_2S , CO or COs and have the average composition SO_2 8.4, O_2 1.5, CO_2 21.2, N_2 70%.

In a patent (37) on the recovery of S, H_2S , SO_2 from materials containing sulfur, e.g. pyrites and anhydrite, the following method has been adopted. Pyrites is passed through a rotary furnace divided into 3 zones: in the first, S is liberated by the hot gases from the later zones; in the second, combustible gas, e.g. water gas and a deficiency of air are admitted to heat the ore and liberate H_2S by the action of the steam formed by combustion; in the third, air and steam are introduced to roast the residue to Fe_2O_3 and liberate the rest of the S as SO_2 which reacts with the H_2S to give S. Anhydrite is treated similarly except that it is mixed with finely ground coal to reduce the $CaSO_4$ to CaS , which is then decomposed by the steam.

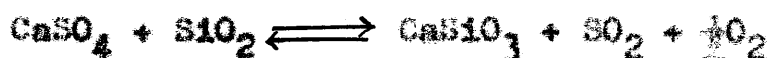
Trifonov (121) in his studies on the easy expulsion of SO_2 from $CaSO_4$ - CaS mixtures by Fe_2O_3 , at high temperatures, maintains that the favourable action of Fe_2O_3 is due to the avoidance of the sulfatisation of CaS by SO_2 .

Schenck and Hammerschmidt (110) studied the equilibrium constant for the reaction $CaS + 2SO_2 \rightleftharpoons CaSO_4 + S_2$ and plotted the isotherms at $850^\circ C$.

In 1934 Charmandarian and Wartschenko (41) heated the mixtures of $CaSO_4$, clay, and carbon in fireclay crucibles and found that fusion took place at 1200° , owing to corrosion and dissolution of the fireclay; the cement so obtained was found to be unsatisfactory. Crucibles lined with Al_2O_3 are refractory and the mass does not fuse after heating during 4 hours at 1450° , the

product contains 15 - 25% SO_3 , but no CaS and yields good cement. The problem of lining was also studied by Budnikoff, Shicharevitsch and Lukova (37). According to them, the ovens should be lined with well fired fireclay brick containing not less than 40% SiO_2 and of a porosity of not less than 8%, the brick should shrink by not greater than 0.5% after refiring for 2 hours at 1450° . Black Dinas is suggested as a possible substitute. Wasilewski and his colleagues (126) in their work on the production of SO_2 and Portland cement from gypsum found that 75% of the CaSO_4 is decomposed to yield Portland cement and SO_2 , by heating for 15 minutes at 1150° with 10% coke and a mixture of oxides (SiO_2 + Al_2O_3 with 1.5% of Fe_2O_3). The work was done on a technical scale, using a continuous process rotary oven and charging a mixture of CaSO_4 17.2, clay 1.62, Fe ore 0.38 and coke 1.72 parts at an optimum rate for the given apparatus. 75% decomposition is attained at 1210° , with a content of 3.5% SO_2 in the issuing gases, and of 4% CaS and 24% CaSO_4 in the product.

Zawadzki and Sobieraj (135) in their work on the decomposition of gypsum found that Portland cement of good quality and not containing CaS or CaSO_4 can be obtained by firing a mixture of CaSO_4 , clay and coke (6%) under conditions analogous to those applied to the production of Portland cement from CaCO_3 , but at a higher initial temperature (1100° - 1200°). The heat of reaction during the formation of mono-calcium silicate from gypsum and silica was found by Honus (66). The value calculated from G. Marchal's partial pressure data for the reaction



was 93, 828 Kg - cal/mol, compared with the value of 92,373 Kg.cal from the Harnst equation. The heat of the formation of the silicate from the two oxides is then 21.7 Kg-cal/mol as the average of the two methods of calculation.

The microscopical study of clinker derived from gypsum was done by Manuilova and Kojak (75), which showed that the petrographic structure of the correctly burned clinker is identical with that of ordinary Portland cement. A considerable quantity of an amorphous substance is also present. The formation of β dicalcium silicate is due to defects in the burning process.

Teraschkevitch and E ventski (77) found that quantitative conversion of CaSO_4 into CaS is achieved by heating with anthracite, coal, CO or H_2 (1 hour at $900 - 1000^\circ$). The product should be cooled in a reducing atmosphere or with water as partial re-oxidation to CaSO_4 takes place in air.

Veidemanis (73) in his studies on the extraction of sulphur from gypsum reduced it at $650^\circ - 1100^\circ$ with coal, anthracite, coke, peat, and wood charcoal. Coal was the most efficient, complete reduction taking place in 30 minutes at 1000° with a mixture corresponding to $\text{CaSO}_4 + 3\text{C}$. With anthracite and peat the efficiencies at 1000° were 95% and 50% respectively. The catalytic effect of Cr_2O_3 enabled the reaction temperature to be lowered by 100° . The catalytic effects of Al_2O_3 ,

Fe_2O_3 and MnO_2 were also investigated, 95% efficiencies at 900° being attained by their use.

Mirew (90) in his work on reduction of CaSO_4 with metallic iron prepared mixtures of CaSO_4 with four equivalents of Fe in a stream of N_2 up to 600° , the reaction was



from $600^\circ - 900^\circ$ the products were CaO , $\text{FeS} + 3\text{FeO}$, and beyond 900° they were CaO , $\text{FeO} + \text{FeS} + 2\text{FeO}$. Some Fe_3O_4 was produced between 600° and 1200° , by the side reaction $\text{CaSO}_4 + 3\text{Fe} = \text{CaS} + \text{Fe}_3\text{O}_4$. Only traces of SO_2 were evolved. Rudnikoff and Rivlin (36) decomposed gypsum with carboniferous pyrites and silica in the ratio 8 : 2 : 1 by heating in a rotary oven, with an air supply such that the combustion temperature is $1000^\circ - 1100^\circ$; >80% of the S is evolved as H_2S and SO_2 under these conditions and the residue contains, approximately, CaS 2, FeS 0.5, and CaSO_4 1.6%.

Pavlov and his colleagues (102) heated a mixture of gypsum, clay and coal in a rotary furnace at $1300 - 50^\circ$ and found that it gives off 88 - 9% of its sulfur as SO_2 and H_2S . These pass into a cooler zone at $600^\circ - 700^\circ$, and deposit 85 - 90% of their S as the free element. The residual clinker satisfies the standards for cement.

In 1941 Newman (100) studied the behaviour of CaSO_4 at high temperatures. Petrographic and X-Ray

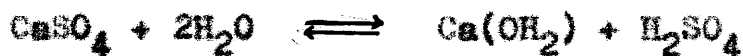
analysis showed a β to α transition of CaSO_4 at 1214°C , but the higher temperature form was unstable and could not be studied at room temperature. An eutectic mixture of CaO and $\alpha\text{-CaSO}_4$ which melted at 1365° was reported. Although compounds, corresponding to the formulae $2\text{CaO}.\text{SO}_3$ and $3\text{CaO}.2\text{CaSO}_4$ have been reported, their presence was not confirmed by this work.

Huttig and Bischoff (68.25) in their work on the decomposition of gypsum by silica found that $\text{CaSO}_4.2\text{H}_2\text{O}$ lost its water when heated to 800° . Further heating at $1000 - 1300^\circ$ with an equimolar amount of SiO_2 caused decomposition of the CaSO_4 . The heating was done in a platinum vessel in an oven with temperature controlled to $\pm 2.5^\circ$. Of the dried gases tried, SO_2 allowed the least decomposition, when a stream was led through the oven at 2 or 4 l/hr, O_2 , air and N_2 allowed somewhat more decomposition. A stream of steam moving at 4 l/hr allowed 92% decomposition after 4 hours at 1100° . According to Bischoff (26) in mixes of CaSO_4 and SiO_2 , air and O_2 influence the equilibrium markedly while N_2 and A are completely inert. Water vapour acts with increasing partial pressure, catalytically promoting the reaction.

Steward (116) in 1943 gave an illustrated description of the mining of anhydrite at Billingham. Its utilisation in the manufacture of H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, cement and nitrochalk fertiliser is shown in flow sheets.

In 1944 Briner and Knodel (30) studied the

thermal decomposition of CaSO_4 in presence of water vapour at more than 1000°C . With artificial CaSO_4 , 80% decomposition can be obtained at $1280 - 1300^\circ$ if water vapour is circulated over the CaSO_4 . If air is used in place of water vapour the decomposition falls to 16%. Experiments were also carried out with natural anhydrite containing 98% CaSO_4 . After heating for four hours at 1300° in a current of water vapour, there was 90% decomposition. CaSO_4 itself decomposes at a reasonable rate only at temperatures $> 1450^\circ$, so that the use of water vapour brings about a fall of not less than 150° in the decomposition temperature. The mechanism of reaction is discussed. It is assumed that hydrolysis of CaSO_4 occurs, this being justified by the fact that superheated water will even hydrolyse NaCl . The reactions occurring are



The resultant reaction is practically



In 1945 Briner (29) calculated free energies and equilibrium constants for the decomposition of CaSO_4 alone and in the presence of SiO_2 and found that the results calculated by the method of Wernst or from tables

of entropied do not agree well with the data of Marchal (J. Chim. phys. 23,38(1926)).

Briner and his co-workers (31,32) also studied the dissociation equilibrium of CaSO_4 alone or in presence of silica, Kaolin and three types of bauxite from $400^\circ - 900^\circ$ in atmospheres of pure N_2 , H_2O and $\text{N}_2 - \text{H}_2\text{O}$ mixtures. In all cases the addition of water vapour, metakaolin, silica or bauxite increases the percentage reacted.

In 1947 Zawadzki and Weychert (136) reviewed the results of semitechnical and technical scale experiments, carried out before the war by the authors, with some details of the process. The CaSO_4 content in some of the clinkers obtained was less than 1.5%. Tensile and compression strength tests gave better results than those prescribed by Polish specifications for cement.

In 1949 Kühne (72) published his work on the production of H_2SO_4 from Gypsum. A ground mixture of gypsum or anhydrite, clay and coke is heated in a magnesite lined furnace. At 700° the reaction $4\text{CaSO}_4 + 2\text{C} = \text{CaS} + 3\text{CaSO}_4 + 2\text{CO}_2$ begins followed by $\text{CaS} + 3\text{CaSO}_4 = 4\text{CaO} + 4\text{SO}_2$ and finally the CaO reacts with the clay. The clinker is suitable for cement and free from CaS and CaSO_4 , if the proportion of C added is exact and uniformly mixed. In large units with convenient supplies of gypsum, SO_2 can be produced competitively with that from pyrites.

Cathala (37,40) describes an electric furnace used in the preparation of H_2SO_4 from CaSO_4 . Pure SiO_2 or bauxite is used as flux. The possible extension of

the process to preparation of Al and cement for European reconstruction is considered. Gavanda (59) in his paper mentions that the extraction of SO_2 from gypsum for the production of H_2SO_4 is carried out mainly by the following methods embodied in several German and French patents: (1) Decomposition of gypsum, by heating at 1400° to $\text{CaO} + \text{SO}_2 + \text{O}$. (2) Reaction with coal according to $\text{CaSO}_4 + \text{C} = \text{CaO} + \text{SO}_2 + \text{CO}$ or $\text{CaSO}_4 + 2\text{C} = \text{CaS} + 2\text{CO}_2$ from which $\text{CaS} + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 + \text{H}_2\text{S}$; this gives SO_2 or S by one of the known methods. (3) Reaction with silica according to $\text{CaSO}_4 + \text{SiO}_2 = \text{SiO}_2\text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2$. The temperature at which disintegration begins decreases from 950° at 5% SiO_2 to 757° at 35% SiO_2 . (4) Reaction with Al_2O_3 at about 935° . (5) Disintegration of gypsum or anhydrite with addition of coal, SiO_2 and Al_2O_3 .

In 1951-52 many reviews appeared on the production of cement and H_2SO_4 from gypsum by Manning (76, 77), Akerman (5), Waesser (125), Higson (62) and Edward (47). Manning (77) describes the location and geological origin of anhydrite and gypsum in England. With a production scale of at least 50,000 tons H_2SO_4 annually and a nearby suitable source of raw materials, acid is made from anhydrite at appreciably less cost than from pyrites. Raw materials required per ton of H_2SO_4 produced are anhydrite 1.66, coal and coke 2.33, sand 0.13 and ash from coal and coke 0.11 tons. The main line of process consists of the preparation of raw materials, reactions in a rotary kiln, purification of gases, conversion of SO_2 to acid, and conversion of kiln clinkers

to cement. The dried raw materials are ground and mixed to give the required proportion of anhydrite, Al_2O_3 , SiO_2 and CaO entering the kiln which operates at a temperature slightly higher than that of a normal cement kiln. Probable course of the reaction is the reduction of anhydrite with coke to form CaS , decomposition of anhydrite by CaS to form CaO and SO_2 and finally, the reaction of residual CaSO_4 with SiO_2 which also combines with CaO and Al_2O_3 to form cement clinker. Accurate control is necessary to prevent side reactions that have been responsible for lack of success in several previous attempts to produce H_2SO_4 from anhydrite. Another review in 1952 by Bedwell⁴⁹ gives the mechanism of reactions, development of process, production and preparation of raw materials, production of SO_2 and clinker, purification of SO_2 , conversion of SO_2 to H_2SO_4 , conversion of clinker to cement, raw material costs, capital costs, production costs and occurrence of CaSO_4 minerals in Great Britain.

Fuji (55) in 1952 decomposed gypsum by kneading it with 15% H_2O , pressing into 15 x 7 mm discs and roasting on a Mg plate painted over with ZrO_2 dust with a neutral or oxidising flame in a gas furnace. It began to decompose to form CaO at $1020 - 50^\circ$, but decomposed in a reducing flame from 850° to CaO and CaS . In an electric furnace the decomposition began at 1350° , partially fused above 1400° and freed only 1.4% CaO at 1450° after 2 hours, the liquid formed apparently retarding the decomposition (Eutectic point of $\text{CaO} - \text{CaSO}_4$ is 1365°).

Nadachowski (78) in his article on the rotary

kiln lining in the production of H_2SO_4 and cement clinker from anhydrite gives the chemical corrosion factors in working conditions of the process of anhydrite decomposition in a rotary kiln and the properties of commercial brands of fireclay and basic refractories to be used in the lining. He recommends using fireclay containing more than 40% Al_2O_3 for lining the heating and cooling regions of a rotary kiln and the lining of the firing region should consist of basic refractories ("Radex A" or "Ankral" type) resistant to constant changes in temperature. The Polish basic refractories (stabilised dolomite, forsterite and magnesite) are not sufficiently resistant to temperature changes, however, stabilised dolomite is the most resistant to corrosion of all lining materials.

Franklin and Pace (52) generate sulfur vapour and gaseous SO_2 in retorts from a charge containing CaSO_4 silicious and/or argillaceous material and coal or charcoal. Any form of CaSO_4 can be used, but natural anhydrite or calcined gypsum is preferred. To provide the silicious material it is desirable to use a clay which contains SiO_2 and Al_2O_3 in the ratio of approximately 2 : 1 by weight. All materials should be reduced to a particle size of less than 150μ , thoroughly mixed and then granulated with suitable bonding agent to form granules of $1/8 - 1/4$ in. Molar proportions of CaSO_4 : C : SiO_2 : Al_2O_3 should be about 1 : 1 : 0.5 (with anthracite fines) and 1 : 1.18 : 0.5 (with bituminous coal). The mix is charged into vertical retorts and heated to $1000-1300^\circ$. To cool the solid residue leaving the bottom of the retorts and also to improve the rate of

reaction, water (about 5% of weight of solids) is injected near the bottom of the retorts to form steam. As far as practicable O_2 is not allowed to enter the retorts. An example using granules composed of 69.5% anhydrite, 21.5% clay and 9% bituminous coal shows that 51% of the total S evolved was free S. Desulfurisation was 90%.

II. Patent Digest:-

A digest of some patented processes is presented in the following schedule:-

Refer- ence	Raw Material	Temp- era- ture	Atmos- phere	Remarks
Basset (17, 18, 19, 20, 21).	1580 K.g $CaSO_4$ + 350 K.g clay + 125 K.g char- coal and 2% iron oxide in (21)	900° for pro- duc- ing SO_2	oxidis- ing	Steam is used in (17). COS is burned to SO_2 in (18) and (19). Air inlets provided at the rear of the furnace.
Bambach (14, 15)	Alkaline earth sulphates	High	Air and water	Meant for oxidised sulphur.
Bambach (16)	$CaSO_4$	High	1.coal gas + air 2.steam C, Fe or S and heated.	$CaSO_4$ was alter- natively mixed with metal sulphide or

Refer- ence	Raw Material	Temp- era- ture	Atmos- phere	Remarks
Metall- bank & Metall- urgische (86)	CaSO ₄ and coal. The height ad- justed in a way that no free O ₂ is present in escaping gases.	-	Air	Free O ₂ subsequen- tly added for oxidation.
Muller & Glinge- stein (97)	Calcium sulphate mixed with alum- inium silicate, silica and carbon less than 1/10th of the weight of calcium sulphate.	Sint- ering point	oxid- ising	-
Weeren (129)	Gypsum + reduct- ion materials + fluxes in pieces of 30 m.m. dia- meter.	-	-	-
Badische Anilin & Soda Fabrik (9, 12)	Gypsum + fuel (In 22), water free raw mater- ial is used.	-	Air	The gases are passed over cata- lysts of fire proof masses soaked with Fe Salt solu- tions to free them from S.

Refer- ence	Raw Material	Temp- era- ture	Atmos- phere	Remarks
Badische Anilin & Soda Fab- rik (13) (10)	do.	do.	CO or gener- ator gas in (10) and/or O ₂ in (13)	glowing coke or coal is used.
Badische Anilin & + fluxes & Soda Fabrik (11)	Gypsum + fuel	-	Air	Reaction carried out in shaft furnace.- SO ₂ is reduced to S by passing through the deep charge.
Tetens (119)	CaSO ₄ + SiO ₂	-	-	Process used for hydraulic cement. Compounds of Ba, Sr and Pb used to combine with un- decomposed sulphate.
Rhenania (104)	Gypsum + SiO ₂	1100°C	Steam and inert gas	

Refer- ence	Raw Material	Temp- era- ture	Atmos- phere	Remarks
Kunze & Sotter (73)	CaSO_4 + sili- cates and aluminates	-	-	Avoidance of fusion not necessary in sintering operation for pro- ducing cement. Clinker can be cooled, granulated and ground.
Rothe & Brenck (108)	Gypsum + SiO_2	above 1100°	oxid- ising	Heating gases are used containing 15% steam.
Farbenind (48)	Gypsum or anhydrite + clay and coal	-	-	Bricks are made before firing.
Harris (60)	CaSO_4 + sand + clay	-	-	Dry powder blown through nozzles in the kiln. Gases freed from dust by vortex or electri- cal separators.

Refer- ence	Raw Material	Temp- era- ture	Atmos- phere	Remarks
Mauris (88,89)	CaSO_4 + clay + C + metallic carbonates, e.g. chalk	-	-	Carbonates used to free the clinker from CaS
Chaval- ier- Girard (43)	Gypsum or CaSO_4 + charcoal	red heat	-	CaS formed treated with CO_2 in pre- sence of water forming H_2S and CaCO_3 . H_2S burned with air to form SO_2
Fleck (51)	Gypsum or anhydrite	10500- 1300°	reduc- ing flame of coal gas & producer gas with insuff- icient air	No dead burnt line or CaS formed

Refer- ence	Raw Material	Temp- era- ture	Atmos- phere	Remarks
Marks (85)	Gypsum + alum- inous material + excess of redu- cing agent	-	-	Granules of raw material are used preventing caking on furnace walls.
Charrin (104)	Gypsum 80.55% Schist 10.06% Coke 5.36% Recovered dust 4.02%	-	-	-
Seailles (112)	CaSO_4 or a mixture of CaSO_4 and aluminous or silicoalumin- ous ore	a) 800° to 900° b) 1000 to 1500°	a) reduc- ing b) oxid- izing	-
Wilson (131)	Finely ground gypsum + finely ground argill- aceous materials is heated to re- duce the partic- les size. The clinker is ground with coke or carbonaceous	-	oxid- izing	Cement and SO_2 is produced.

Refer- ence	Raw Material	Temp- era- ture	Atmos- phere	Remarks
Wilson (cont'd)	material containing $\text{SiO}_2, \text{Al}_2\text{O}_3,$ or $\text{Fe}_2\text{O}_3,$ proportional to give the right compos- ition			

III. Important Aspects of the Decomposition of Gypsum:-

Measurement of the sulfur dioxide gas pressures obtained by the heating of gypsum alone indicate that without the use of fluxes and a reducing agent, the process cannot be employed economically. Even when CaSO_4 is almost molten at 1400°C , the vapour pressure equilibrium shows a maximum of 7% in the gas phase (80).

Zawadski (133) found that the total gas pressure above natural anhydrite at 1180°C was 2.4 mm.Hg rising to 31 mm at 1340°C , and to 47.5 mm at 1370°C . If SO_2 is obtained by decomposing gypsum at its melting point,² chemical engineering problems of great magnitude would have to be faced.

The published work on calcium sulphate has been done on samples obtained by the ignitions of synthetic gypsum. It is known that dehydrated gypsum is more easily decomposed than natural anhydrite in laboratory experiments, giving considerably higher decomposition pressure (80,133).

The thermal decomposition of CaSO_4 can be represented by the following equation

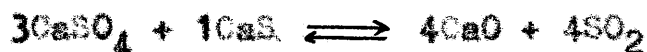


It was shown by Hofman and Mostowitch (64) that the thermal decomposition of CaSO_4 is accelerated by the presence of SiO_2 and Fe_2O_3 which combined with the CaO produced and promoted the forward reaction. Alumina also was found to have similar effect later on. As according to Marchal (80) the reaction between SiO_2 and CaSO_4 is less endothermic than the thermal decomposition of CaSO_4 alone, the reaction would proceed at lower temperatures. Neumann (99) showed that the decomposition pressure is increased appreciably by ferric oxide, considerably by silica and very much by kaolin.

It is also to be remembered that ignited silica will be more reactive than the non-ignited one. Although the fluxes help the decomposition, their effect is too small to make sulphuric acid production, an economic proposition, unless a reducing agent is added. The reaction can be represented as follows:-



and is complete below 1000°C . Hofman and Mostowitch (65) studied the reaction between CaSO_4 and CaS in dry air and found that the reaction began at 800°C and became rapid between 850 and 900°C . Due to the presence of oxygen, the oxidation of CaS to CaSO_4 was more rapid than the reaction:-



which according to Neumann (99) could only be carried to completion at 1000°C , in a stream of pure N_2 .

Zawadzki (133) studied the reaction in the absence of air and measured the total pressure due to SO_2 and S vapour in this system. It was found that up to 1100° the total pressures were relatively small - at 1120° the total pressure only little more than one third atmospheric pressure. It was concluded that the lower the temperature the greater was the ratio of elemental sulfur to total. Schenck and Hammerschmidt (110) found that in the reaction $\text{CaS} + 2\text{SO}_2 \rightleftharpoons \text{CaSO}_4 + \text{S}_2$ (a) at any given total pressure the proportion of S is greater, the lower the temperature and (b) at any given temperature the proportion of S in the gas phase is greater, the greater the total pressure.

The literature survey thus shows that if calcium sulfate is mixed with carbon and fluxes, both cement clinker and sulphuric acid can be produced. It is necessary therefore to determine the correct proportions of the raw materials, as the quality and quantity of the products are directly affected by them.

The stage has been reached where further advances depend upon the study of time temperature relationship and understanding the mechanism of reactions at temperatures, at which the kilns are operated, using the raw materials available to the industry.

CHAPTER III.

THERMODYNAMICS OF POSSIBLE REACTIONS.

As a preliminary to the consideration of the kinetics of the reactions being studied, a review of the thermodynamics of the more probable reactions was undertaken. While thermodynamics can give no idea of the rate at which various reactions will proceed, it is possible that, in some cases thermodynamic calculations might indicate that the degree to which any reaction could proceed is negligible.

Any conclusions based on such calculations must be made with care since equilibrium is unlikely to be reached in the systems where gaseous products are removed continuously.

In the case of reactions involving only solids, it must be borne in mind that, if the reactants and products have not an appreciable mutual solubility, their thermodynamic activities remain constant throughout the course of the reaction. Thus, such reactions cannot reach equilibrium. In fact the reactions seldom reach completion because some of the solid particles are not in contact with another reactant. This does not represent attainment of true equilibrium. The reaction will proceed in the direction in which there is a negative free energy change, but where an equilibrium constant is calculated from the free energy change for these reactions, it can only be taken as an indication of the direction in which the reaction will proceed.

Reactions, concerned with thermal decomposition of

calcium sulfate are the reduction of calcium sulphate, interaction of calcium sulphate with the products of decomposition, or of the products with the atmosphere. The more important reactions which may play a part are considered below.

A. Thermal Decomposition of Calcium Sulphate:-

The probable reactions in the thermal decomposition of calcium sulphate have been studied by a selection of equations.

The equilibrium constant K of a reaction at any temperature T may be found from the standard free energy change G° of the reaction at that temperature.

$$\text{The relationship is } \left(\frac{\Delta G^\circ}{T} \right)_T = -R \ln k$$

If $\left(\frac{\Delta G^\circ}{T} \right)_T$ is expressed in cal/g mole $^\circ K$

the equation becomes

$$4.576 \log_{10} K = - \left(\frac{\Delta G^\circ}{T} \right)_T$$

where $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

The equations are as follows:-

(a) Neutral or Oxidising Conditions:-



$$\log K = -\frac{25,600}{T} + 10.58 + 1.681 \log T$$

$$-1.005 \times 10^{-3}T - 0.0693 \times 10^{-6}T^2$$



$$\log K = \frac{-20,750}{T} + 10.45 + 1.181 \log T -$$

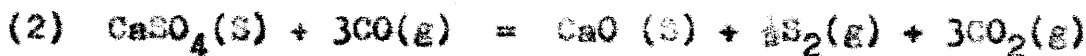
$$0.80 \times 10^{-3}T + 0.1165 \times 10^{-6}T^2$$

(b) Reducing Conditions:-



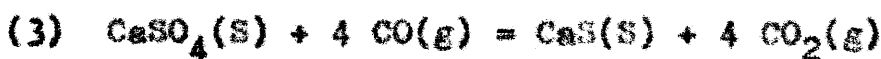
$$\log K = \frac{-11,000}{T} + 9.26 + 0.442 \log T - 0.47$$

$$\times 10^{-3}T - 0.0731 \times 10^{-6}T^2$$



$$\log K = \frac{2,835}{T} + 7.65 - 0.969 \log T + 0.236$$

$$\times 10^{-3}T - 0.221 \times 10^{-6}T^2$$



$$\log K = \frac{9,040}{T} + 7.64 - 2.292 \log T + 0.716$$

$$\times 10^{-3}T + 0.29 \times 10^{-6}T^2$$



$$\log K = \frac{23,800}{T} - 1.29 - 1.009 \log T + 0.38 \\ \times 10^{-3}T - 0.0328 \times 10^{-6}T^2$$



$$\log K = \frac{-53,100}{T} + 30.25 + 4.06 \log T \\ - 2.58 \times 10^{-3}T - 0.31 \times 10^{-6}T^2$$

$\frac{\Delta G^\circ}{T}$ was derived in cal/(gm.mol)(°K) using the expression

$$4.576 \log_{10} K = - \left(\frac{\Delta G^\circ}{T} \right)_T$$

Heat of reaction at 18°C for selected reactions is as follows:-

Reaction no.	18°C cal/g.mol	Heat required Btu/ton sulfur based on 18°C
a(1)	117,800	13,210,000
b(4)	- 109,500	-12,300,000
b(5)	244,100	6,850,000

B. Thermal decomposition of Calcium Sulphate in the Presence of Various Additives:-

The presence of various oxides causes CaSO_4 to decompose more readily. Marchal (78,80) has measured the

decomposition pressure of mixtures of calcium sulfate and some oxides in a closed system. The following table has been prepared by Heumann (99) based largely on Marchal's work.

Mixture of CaSO ₄ with	Pressure m.m. Hg.						
	940	1000	1100	1170	1240	1250	1280
SiO ₂	105	20	94	219	-	575	877
Al ₂ O ₃	-	9	25	50	-	133	200
Kaolin	7.5	17.3	58.9	1,070	-	-	-
Fe ₂ O ₃	-	12.5	37	90	178	-	273

Reaction of CaSO₄ with Silica:-

Eriner (29) calculated the free energy change in the reaction $\text{CaSO}_4 + \text{SiO}_2 = \text{CaSiO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2$. He obtained the expression

$$\log K_p = - \frac{93,100}{4.57 T} + 1.5 \times 1.75 \log T + 4.7$$

$$\text{where } K_p = P_{\text{SO}_2} \cdot P_{\text{O}_2}^{\frac{1}{2}}$$

A comparison of Eriner's calculated values and the experimental values of Marchal and Eriner at 1300 and 1500°K are as follows:-

°K	Calculated P	Measured total Pressure P	
		Marchal	Eriner et al
1300	154	34	11.1
1500	2650	440	42.4

Whereas the calculated and experimental values for equilibrium pressures of CaSO_4 , alone, agree reasonably well, the corresponding values in the presence of silica diverge widely.

Briner concluded that the reaction upon which the calculation was based is not the main one taking place.

Complete data is not available for the reaction involving 2SiO_2 , but Briner shows that it will be considerably more endothermic, than that with one equivalent of silica, i.e. consideration of this reaction will bring the calculated pressure much nearer to the experimental value.

Some of the more important conclusions of the thermodynamic study are:

1. The reaction $\text{CaS} + 3\text{CaSO}_4 \longrightarrow 4\text{CaO} + 4\text{SO}_2$ is favoured by a higher temperature in the range $1100 - 1300^\circ\text{C}$ becoming significant above about 1170°C .
2. The temperature required for appreciable decomposition of CaSO_4 will be about 1340°C .
3. Reduction of CaSO_4 by CO should begin at about 720°C .
4. Reaction between $\text{CaSO}_4 + \text{SiO}_2$ should begin at about 970°C .

CHAPTER IV.

SOLID-GAS AND SOLID-STATE REACTIONS.

On the basis of the thermodynamic data and previous experimental evidence, it has been found that a number of reactions probably play a part in the processes being studied. Some of these are gas-solid and solid-solid reactions. It is, therefore, proposed to discuss the characteristics of these types of reactions to help in establishing the parts played by each.

I. Solid-gas Reactions:-

In order to initiate a solid-gas reaction, the participating molecules must remain in contact at an interface for a sufficient time. The first step is therefore an adsorption of the gas molecule on the solid surface. Catalytic processes involve the adsorption step without further reaction with the surface and much information about the primary step has been obtained from catalytic studies.

Physical adsorption:-

The first stage in the interaction of a gas with a solid involves Van der Waal's forces of which the energy is not very high, being under 5,000 cal/mole for most gases. The physical adsorption being exothermic, the amount of adsorption, due to these forces, decreases with increasing temperature. Calculations show that the amount of physical adsorption is negligible above 600°C. In a few cases

however, the total adsorption is found to increase with temperature, over a limited temperature range. This indicates that, in these cases, other forces of higher activation energies come into play.

Chemisorption:-

These forces of higher energy also give rise to higher heats of adsorption, of the order of 20,000 to 100,000 cal/mole or more. The forces are similar to those, concerned in the formation of chemical bonds and this type of adsorption is referred to as chemisorption.

The forces leading to chemisorption are highly specific, in contrast to Van der Waal's forces. Most experimental work has been done on the adsorption of gases upon metals but Roberts and Anderson (105) have shown that oxygen is very rapidly adsorbed upon uranium dioxide and metallic sulphides, even at room temperature. (6).

In this work we are concerned mainly with the reaction of gases with ionic solids. In such cases, the bonds formed are of such energy that the gas concerned is not reversibly desorbed, but products of reaction are desorbed. Garner and other workers at Bristol (56, 57, 58, 45), found that the reversible chemisorption of CO on oxides at room temperature does not bring about reduction and is believed to take place on cation sites. The irreversible adsorption of CO at higher temperatures is believed to take place on the oxide ions, forming covalent bonds, the oxidised CO being desorbed as CO₂.

II. Solid-State Reactions:-

Irrespective of the number of reactants, solid-state reactions can be considered as being made up of binary reactions because chemical reactions take place at the boundaries between phases. For example, in the formation of such ternary compounds as $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, it is found that two of the three components combine at the first step and then the third component combines with this compound in a second step.

Often, compounds are used which decompose into the three reactants upon heating. The evolution of gases does not usually alter the nature of the reaction. In such cases, the increased reactivity of the freshly formed solid is frequently an advantage. For example, dehydrated gypsum is considerably more reactive than anhydrite.

III. Reaction Kinetics:-

The over-all reaction rates are determined by the following factors.

1. The distribution of phases and the order in which they appear.
2. Processes at phase boundaries, including
 - (a) Transfer of material.
 - (b) Chemical reaction.
 - (c) Formation and growth of nuclei.

3. Diffusion through reaction products.

Two special cases may often be distinguished.

- (i) The phase boundary processes are sufficiently rapid to maintain equilibrium and diffusion in the product layer is rate determining.
- (ii) The phase boundary processes are of a rate comparable with diffusion and diffusing material collects at one of the phase boundaries. In the early stages where the product layers are thin, the effect of diffusion may be negligible.

(a) Thermal Decomposition of a Single Substance:-

The majority of reactions which have been studied are of type



i.e. a new phase B is formed within the lattice of A. Due to the finite size of the molecules a "strain" will be imposed on the surrounding phase A. If work must be done to form the nuclei of B within the matrix of A, the energy must be obtained from the free energy change of the reaction. Then, as for a crystal growing solution, there will be a critical size below which the particle of the new phase is not stable.

(b) Growth of Nuclei:-

During nucleation, the apparent rate of reaction accelerates rapidly. The growth of nuclei, once formed, may follow a first or second order rate law. The characteristics of the growth of nuclei are often hard to distinguish if nuclei are being formed constantly during growth. If, however, nuclei form only at particular points of the crystal lattice, these may be rapidly used up and the rate of change will then be due only to growth of nuclei.

(c) Endothermic Reactions:-

In the case of strongly exothermic reactions, back reaction is usually negligible or at least the equilibrium favours the forward reaction. In the case of endothermic reactions back reaction is often significant in a closed system. Examples of endothermic reactions are loss of water of crystallisation by crystalline hydrates and decomposition of carbonates. The dehydration of gypsum would come under the first heading, although it has not been studied in detail, kinetically. The further decomposition of calcium sulphate by heating would also be endothermic.

When finely ground material is used, as in these experiments, the crystals have been broken extensively so that there are plenty of suitable places from which nucleation can begin. For crystalline materials, the shapes of the nuclei formed are often related to the crystal habit.

All these reactions involve transfer of material across an interface. In the case of decomposition of calcium sulphate, nuclei of CaO are formed within the calcium sulphate and soon a layer of calcium oxide surrounds the particles of calcium sulphate. For further reaction, sulphur trioxide (or sulphur dioxide and oxygen) must be transported through the layer of calcium oxide.

Fischbeck and Snaidt (49) concluded that for many endothermic solid state reactions, the activation energy was equal to the heat of reaction, i.e. the back reactions must occur without activation.

(d) Exothermic Solid Reactions:-

If we limit the discussion here to decomposition reactions, they usually are of the type:



Cases are known of



and



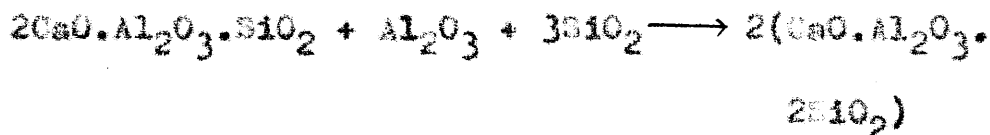
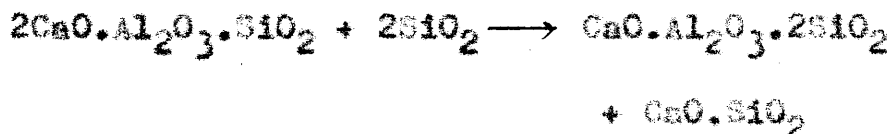
Some of these substances are explosives. As a class they are of minor interest in the present work.

(e) Solid-Solid Reactions:-

In contrast to reactions in fluid phases, solid-state reactions occur between solids, usually crystalline, in which motion of the lattice units is very restricted and is a function of the concentration of defects of various sorts in the crystal lattice.

As mentioned previously, even complex reactions are always made up of a series of binary steps. X-ray powder analysis shows that in the formation of gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), the intermediate products are $12 \text{CaO} \cdot 7\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\beta - 2\text{CaO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$.

Anorthite appears to be formed by further reaction of gehlenite.



As for the decomposition of solids, the reaction of two solids involves mass transfer of one or both reactants through the product layer. Two mechanisms are important:

(i) Diffusion through the crystal lattice:-

This is dependent on the presence of various types of gross imperfections in the lattice.

(ii) "Diffusion" along crystal surfaces and in channels and fissures in imperfect lattices. These surface processes are very dependent on the previous treatment of the system.

It is not established in most cases whether the migrating material moves in the form of molecules or ions.

Tammann suggested that different lattice diffusion processes become operative at temperatures bearing a definite relationship to its melting point. If this ratio is α for the absolute temperatures, surface mobility was said to become significant at $\alpha = 0.3$ and lattice diffusion at $\alpha = 0.5$. For solids in "active" states the ratio may be distinctly lower.

(f) Consecutive Reactions:-

Among the reactions under study, there are several examples of consecutive reactions in which an intermediate product is formed and decomposed



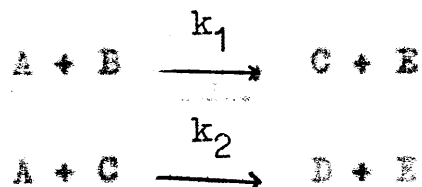
where k_1 and k_2 are velocity constants.

It can readily be shown that under these circumstances the concentration of B will be given by

$$C_B = a \left[\frac{k_1}{k_2 - k_1} \right] \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

(g) Competitive, Consecutive Second Order Reactions:-

As an example of competitive, consecutive second order reactions, consider the complex reaction



with

$$dA/dt = -k_1 AB - k_2 AC$$

$$dB/dt = -k_1 AB$$

$$dC/dt = k_1 AB - k_2 AC$$

$$dD/dt = k_2 AC$$

By material balance there results

$$A - 2B - C = A_0 - 2B_0$$

$$B + C + D = B_0$$

where the zero subscripts indicate initial concentrations, it being assumed that only A and B are present at the start.

Experimental conditions can be so chosen as to make these pseudo-first order reactions. For example, a large excess of A may be used. The integration for such cases is then equivalent to the successive first-order reactions.

CHAPTER V.

EQUIPMENT.

I.

(1) Pellet-making Press:-

To make pellets of $1/2$ " diameter, a pellet making hand-press was designed, as shown in the diagram. After its manufacture, the parts which came in contact with the pellet, were hard-chrome plated, to avoid inclusion of iron, which otherwise was noticeable on the surface of the pellets. This press was ideal for making small batches of pellets for experimental work.

(2) Platinum Boats:-

Ten platinum boats were manufactured by Garret, Davidson & Mathey with the following dimensions:-

Length	Width	Height	Thickness of Material
2 cm	1.5 cm	$3/4$ cm	0.017 inches

These boats contained the pellets which were fed into the reactors for the study of various systems.

II. Reactor Atmospheres:-

(1) Oxidising:-

All work in oxidising atmosphere was done by mixing O_2 and air in the ratio 1 : 10.

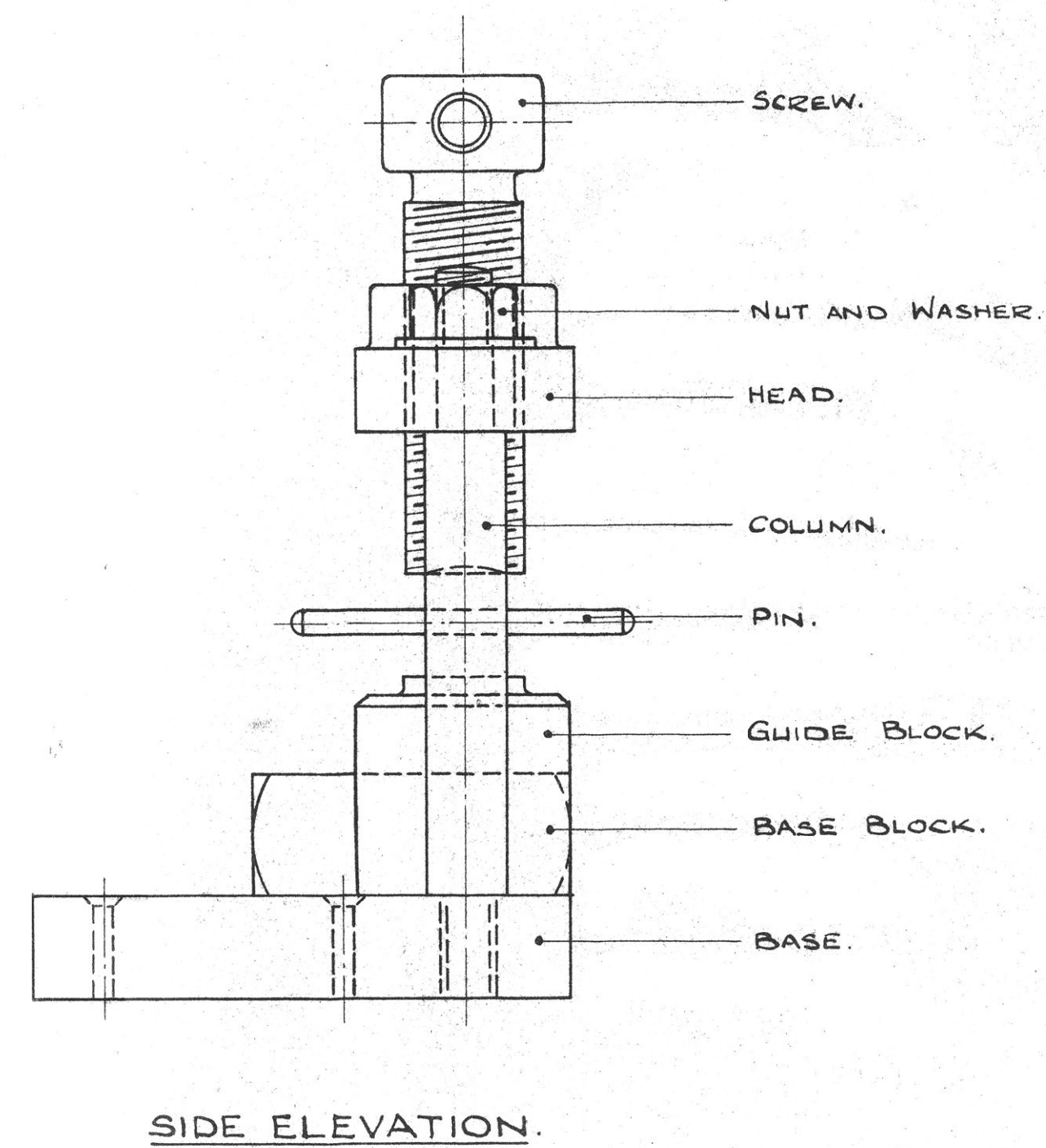
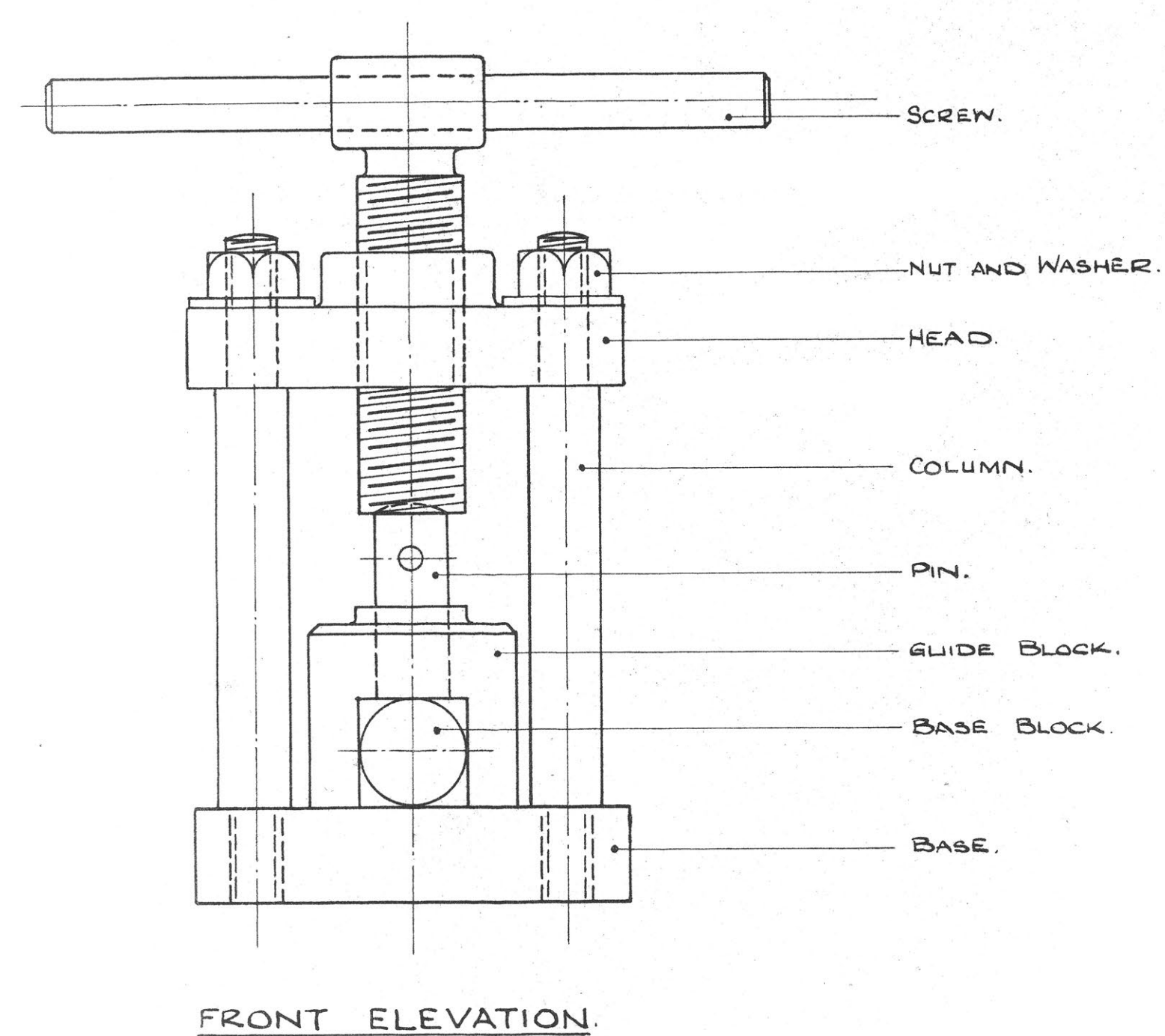
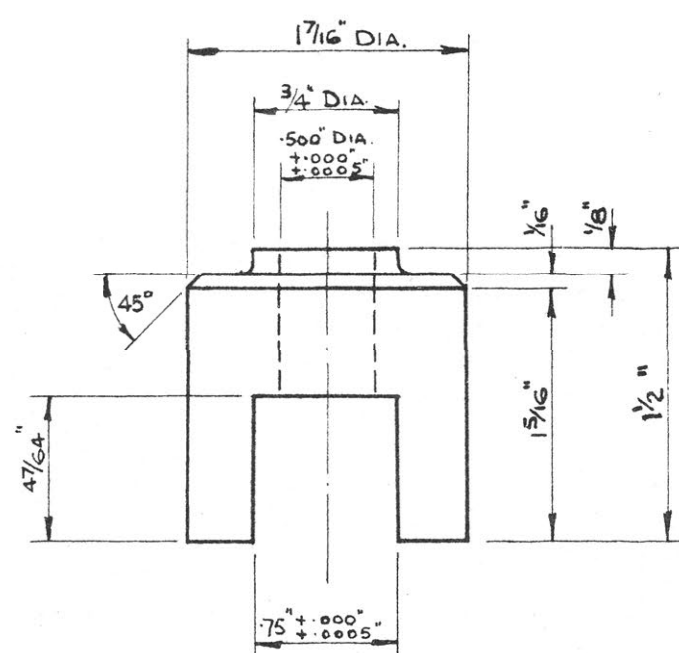


FIG. 5.1.1

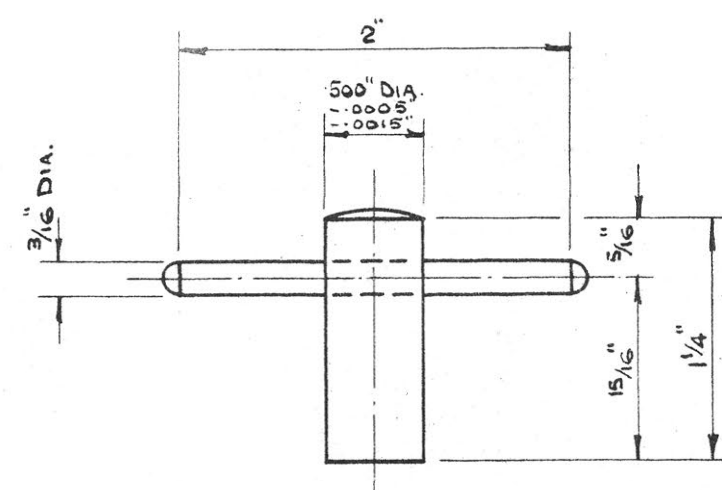
ARRANGEMENT OF PELLET
MAKING MACHINE.

SCALE FULL SIZE DRW. BY. M.S.ZAHID

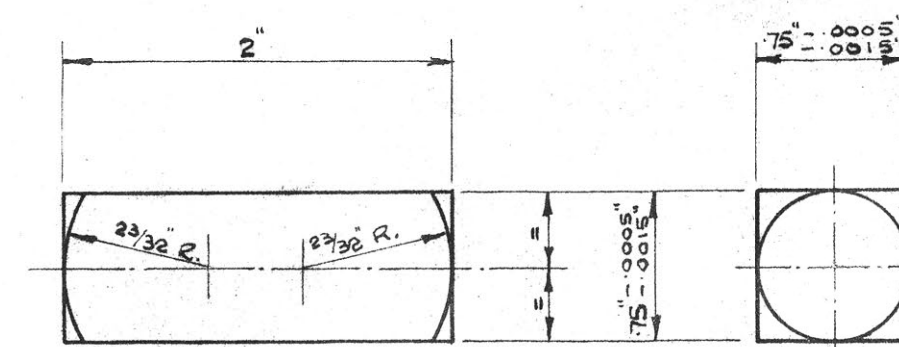
DATE 20.8.56. DRG. N° 1.



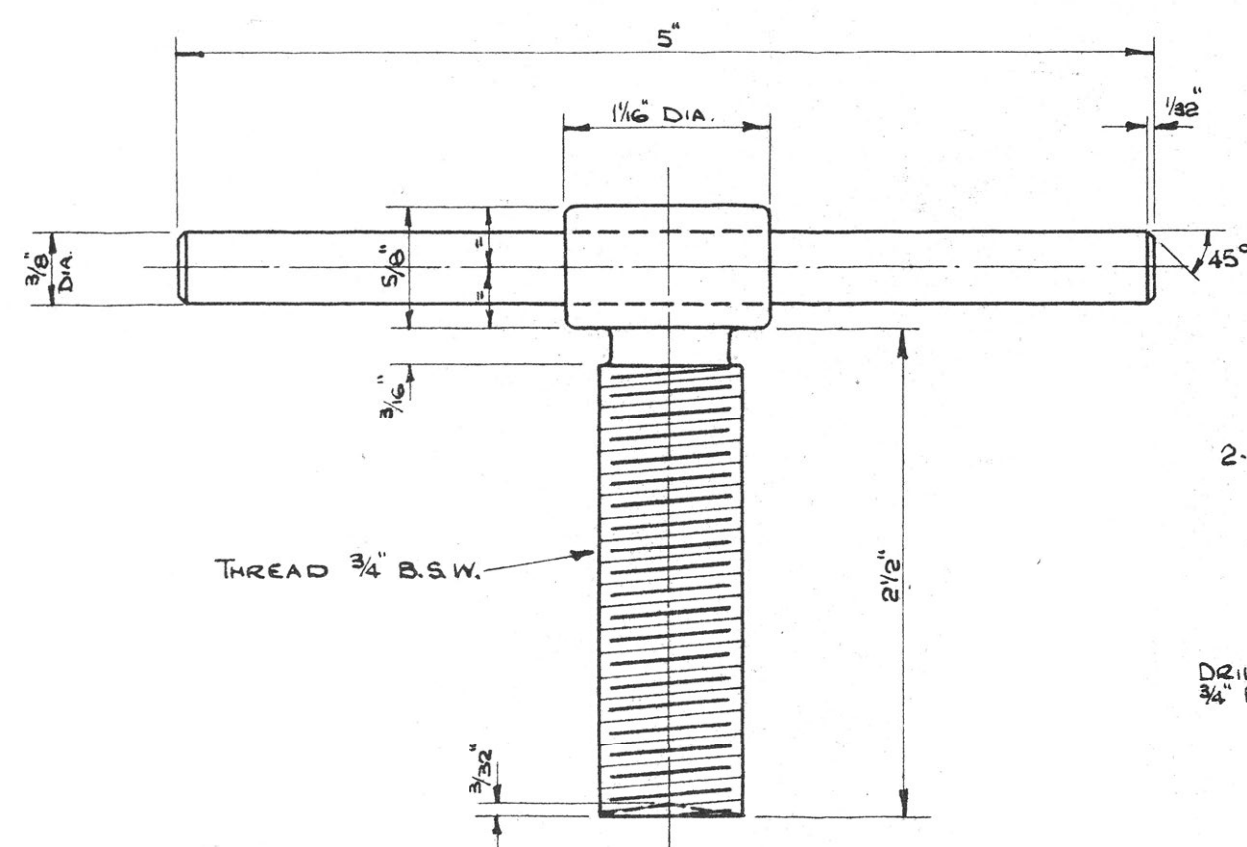
1 OFF AS DRAWN, GUIDE BLOCK.
MAT. STAINLESS STEEL



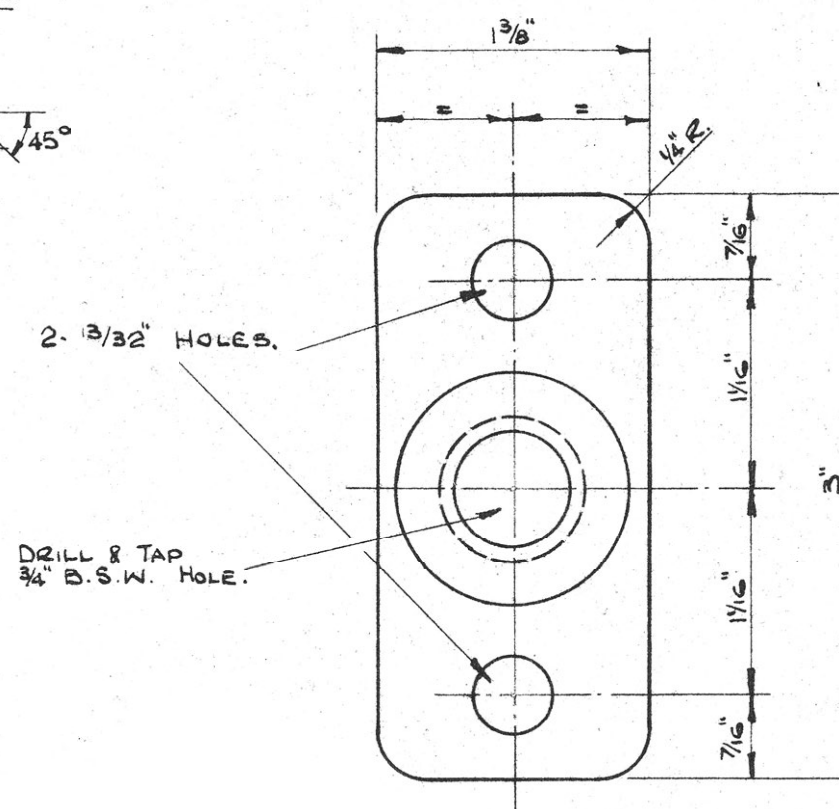
1 OFF AS DRAWN, PIN
MAT. STAINLESS STEEL



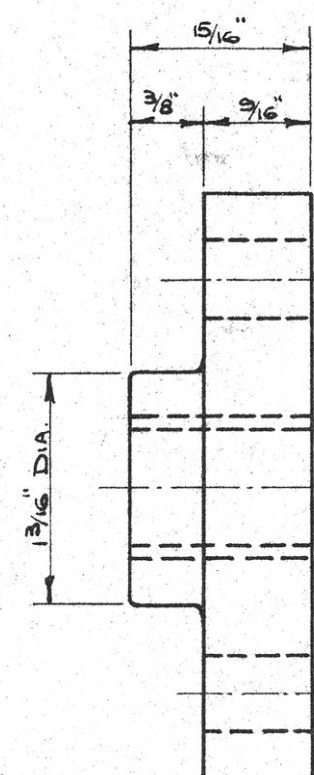
1 OFF AS DRAWN, BASE BLOCK.
MAT. STAINLESS STEEL



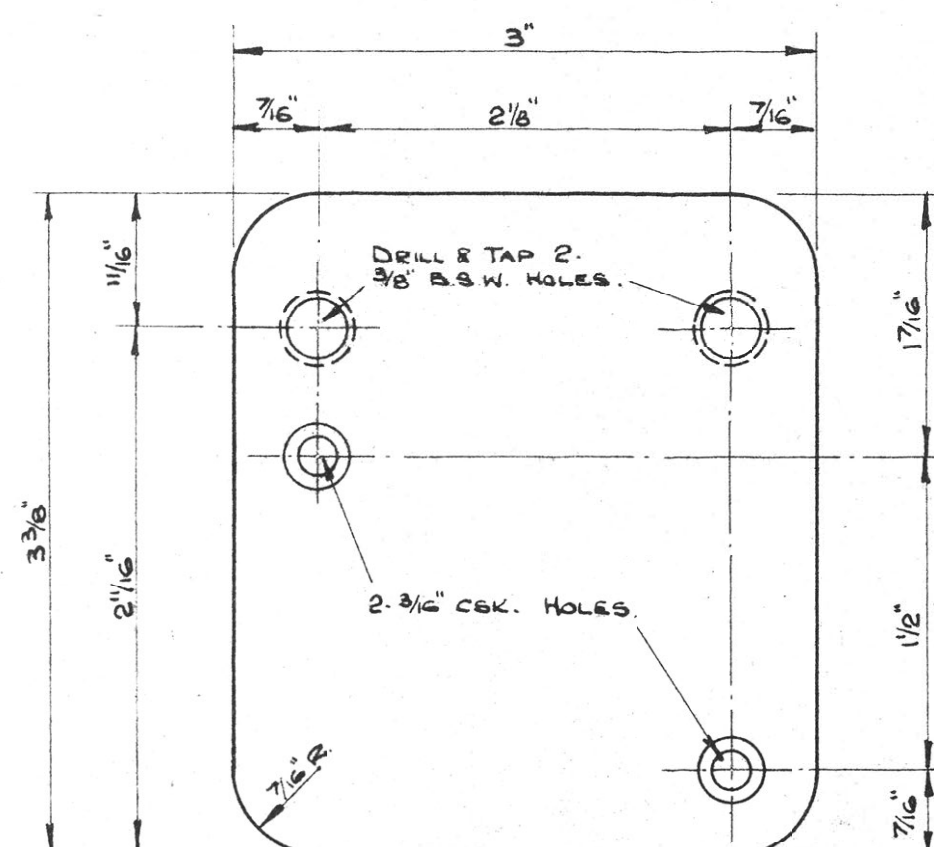
1 OFF AS DRAWN, SCREW.
MAT. HARD CHR. PLATED M.S.



1 OFF AS DRAWN, HEAD
MAT. HARD CHR. PLATED M.S.



2 OFF AS DRAWN, COLUMN
MAT. HARD CHR. PLATED M.S.



1 OFF AS DRAWN, BASE
MAT. HARD CHR. PLATED M.S.

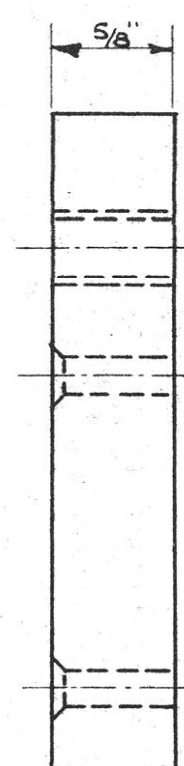


FIG. 5.1.2

DETAILS OF PELLET
MAKING MACHINE

SCALE FULL SIZE	DRW. BY M.S. ZAHID
DATE 20.8.56.	DRG. N° 2.



Fig. 5.1.3
Pellet Making Machine.

(a) Regulation of gases:-

There was considerable fluctuation of pressure in the compressed air service to the laboratory. To get an even flow, an air-regulating valve was used, followed by a needle valve, for accurate adjustment. Minor fluctuations were avoided, by the inclusion of silica gel and P_2O_5 + asbestos U-tubes, which also served to remove moisture from air.

Oxygen was withdrawn from the cylinder, using oxygen pressure reducing valve, followed by a needle valve. The flow was even.

(b) Purification of gases:-

(i) Oxygen was purified, by passing through a bubbler containing conc: Sulphuric acid followed by a U-tube containing ascarite, which is a Sodium Hydrate Asbestos Absorbent (//5).

(ii) The air contained appreciable amounts of CO_2 and dust particles. As both interfered with estimations they were removed by using a CO_2 scrubber, which retained CO_2 and dust particles. The moisture was removed, by interposing a U-tube containing 20% impregnated silica gel and another tube containing a 1 : 1 mixture of P_2O_5 and asbestos fibres.

(2) Non-Oxidising:-

Oxygen free N_2 was used for producing non-oxidising atmospheres. N_2 was obtained from a cylinder.

(3) Description of Scrubber:-

The scrubber employed was very efficient and supplied a continuous stream of purified air. It contained a 20% solution of NaOH. The air was bubbled through an orifice into the spiral and scrubbed by long contact of bubbles with NaOH solution. The stream of purified air not only produced the desired atmosphere in the reactors, when mixed with pure O_2 , but also stirred the liquid in the absorbers, during titrations. It also swept the atmosphere above the liquid free from CO_2 and other interfering gases. Such scrubbers may be used not only for purifying gas streams, but also for drying and controlling their moisture content, at any desired degree of saturation. For the latter purpose the scrubber may be charged with conc: H_2SO_4 , sulphuric acid solutions or saturated solutions of certain salts.

The dimensions were as follows:-

Height of apparatus, cm	65
Upper reservoir:-	
Height, cm	12
Diameter, cm	10
Capacity, ml	500

Lower reservoir:-

Height, cm	20
Diameter, cm	13
Capacity, ml	1000

Cylindrical tube connecting upper and lower reservoir:-

Height, cm	25
Diameter, cm	3.5



Fig. 5.2.4
Scrubber for the removal of CO_2
and dust particles.

Helical tube:-

Length, cm	200
Diameter, cm	0.6
Inlet jet, diameter of orifice, cm	0.1
Maximum aspiration rate, litres/hr.	75

(4) Flow measurements:-

The flowmeters were two feet long, each having a two inch long capillary tube, and a glass bulb in the calibrated arm. To trap any overflow. They were filled with water up to the zero mark, which was lightly coloured with litmus to make the meniscus easily readable. The flowmeters were wired to the supporting wooden boards and suspended on the rack by means of hooks.

The flowmeters were calibrated up to 180 cc/minute gas flow, as this is the maximum limit for the smooth flow of bubbles through the absorbers. The calibration was done, by using Fischer & Porter Flowrator meter using size O8 tube with 1/16" glass ball, for flows from 2 to 59 cc/minute and, 1/16" stainless steel ball for up to 180 cc/minute. The glass ball gives a better range of calibrations within its limits.

The dimensions were as follows:-

Length of the flowmeter	=	2 ft.
Bore of the tube	=	5/32 inches.
Length of Capillary tube	=	2 inches.
Bore of the Capillary tube	=	0.6 mm
Diameter of the bulb	=	1½ inch.
Length of the side arms	=	1½ inches each.
Bore of the side arms	=	1/4 inch.

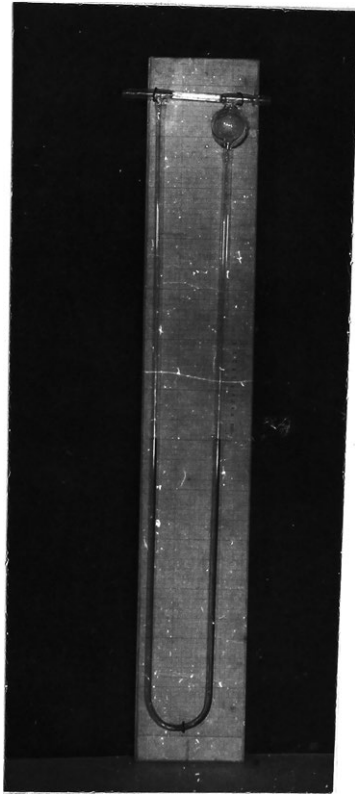


Fig. 5.2.5
Flowmeter.

The bore of the capillary was selected, to give maximum height of water column for the given flows in order to obtain better calibrations.

III. Reactors:-

The requirements for the reactors were as follows:-

1. They should be constructed of materials, which should not be affected by the products of the reactions involved.
2. The refractory tubes used should be impervious.
3. The reactors should be capable of being sealed quickly, to avoid the loss of gases and also to produce any desired atmosphere in it.
4. They should withstand the buildup of gas pressures within the system.
5. Above all they should be capable of producing high temperatures, as the complete decomposition of gypsum takes place above 1400°C .
6. Accurate temperature control should be a desirable feature.
7. The temperature near the middle of the hot portion of reactor should be as uniform as possible.

8. The cost of construction and consumption of current should be a minimum.

Two reactors were built to comply with the requirements. The first one produced temperatures up to 1300°C, and was meant to be used, till the second reactor was designed and constructed to produce temperatures as high as 1700°C.

Design of Reactor A (1300°C):-

Reactor A consisted of a silica tube, wound with Kanthal A wire and lagged with Kieselguhr.

The design considerations and description of various parts are as follows:-

(1) Heating Element:-

It consisted of Kanthal A wire, wound around the silica tube. The most suitable wire diameter was calculated as follows:- (69)

$$d = \frac{1}{335.3} \sqrt[3]{\frac{P^2}{E} \times \frac{t}{p}}$$

where

- d = diameter of wire in inches
- P = rating of element in watts
- t = resistivity in ohms per cir. mil ft. of desired Kanthal alloy at working temperature.
- p = surface load in watts per square inch.
- R = total resistance of element in ohms
- E = voltage

$$\text{i.e. } d = \frac{1}{335.3} \sqrt[3]{\frac{2000^2}{240} \times \frac{887.832}{6}} = 0.064 \text{ inches}$$

$$= 16 \text{ S.W.G.} = 14 \text{ B \& S.}$$

The nearest diameter available was 17 B & S.

$$\text{For resistive A.C. loads } R = \frac{V}{A}$$

$$\begin{aligned} \text{From a 2kVA variac, the current, which can be drawn at} \\ 240 \text{ volts} &= \frac{2000}{240} = 8.33 \text{ amps.} \end{aligned}$$

$$\therefore R = \frac{240}{8.33} = 28.81 \text{ ohms.}$$

$$\text{If there is a 5\% increase in resistance of the wire at } 1300^{\circ}\text{C,} \\ \text{the corrected value of } R = 28.81 \times \frac{95}{100} = 27.37 \text{ ohms}$$

$$\text{Resistance of B \& S 17 Kanthal A wire} = 0.412 \text{ ohm/ft.}$$

$$\text{i.e. Length of wire required} = \frac{27.37}{0.412} = 66.43 \text{ ft.}$$

Thus 66.43 feet of the wire were evenly wound in 87 turns to constitute the heating element. Each turn of the wire was situated at a distance of $5/32$ " from each other, except the outermost turns which were wound a little closer to give an overall length of $13\frac{1}{2}$ " heating element. Before the winding was done a mica and then an asbestos sheet was wrapped around the tube. The asbestos sheet was marked with points where the turns were to come, then moistened and winding completed. The winding^{was} anchored at each end to loops of

Kanthal wire, tightened around the tube and then coated with a thin layer of Alfrax cement no. K5-29 which could withstand temperatures up to 1400°C .

(2) Reactor tube:-

As already stated the $2\frac{1}{2}$ " I.D. tube was made of fused silica. Its outlet end was sealed by welding a silica dish on it. Two holes were drilled by grinding with carborundum and copper tubes in this dish. On one hole a silica tube was welded to act as an outlet for the gases. This tube was ground to fit into a B10 socket attached to the absorber. On the other hole a silica thermocouple sheath was welded. This sheath was made by sealing the end of a silica tube by fusion and extends up to the middle of the hot portion of the reactor tube. To create the desired atmosphere in the reactor, the inlet tube was welded to another hole drilled in the reactor tube near the open end. Inside the reactor, it was bent at 45° towards the centre.

Silica becomes brittle after being heated at high temperatures. It also requires very slow annealing after welding to reduce the danger of cracking and breakage.

All weldings were done using a silica rod and oxy-hydrogen flame.

As the boats containing the pellets of the mixtures to be studied, were to be inserted and withdrawn from the reactor intermittently, there arose the problem of sealing it with an end plate, which could be used to seal this end

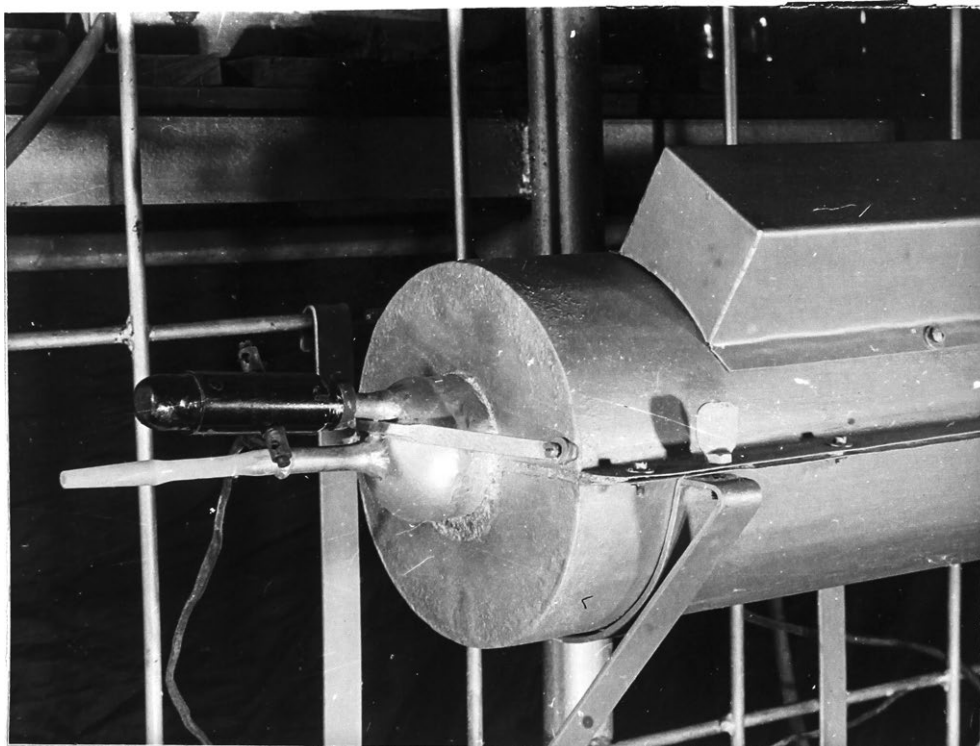


Fig. 5.3.6
Outlet side of Reactor A.

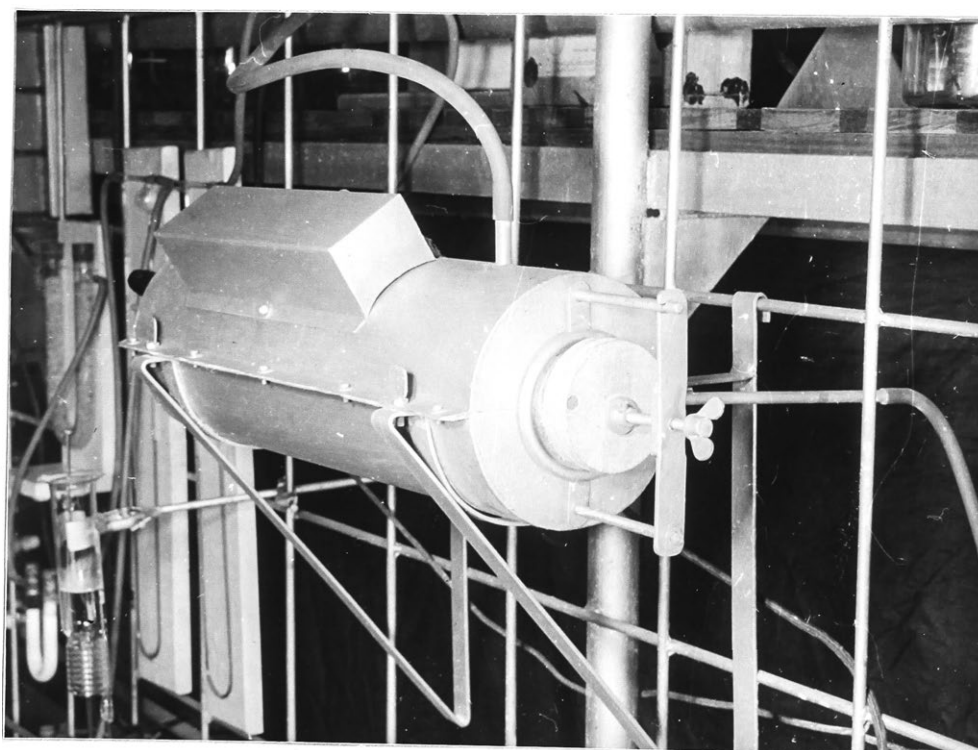


Fig. 5.3.7
Inlet side of Reactor A.

during the time the run was being made. A circular end plate was made from two pieces of 1/2" thick Sindanyo board screwed together, one side of which had a circular groove to contain the gasket.

Various gaskets were used but with the rise of temperature most of them did not work satisfactorily. The gaskets tried were made of

- (i) Neoprene.
- (ii) Salamanderite.
- (iii) Klingerit 1000. C.A.F. 178 type which is made of 1/8" thick compressed asbestos fibre, jointly graphited with sheet gauze and used when friction or high stress is encountered.
- (iv) Shim brass lubricated with Ragosine Molyoil grease 44.
- (v) Asbestos papers lubricated with silicone grease.
- (vi) Silicone rubber.

Silicone rubber gasket coupled with the air cooling of the end of the tube proved satisfactory. Normally the other gaskets would work provided the end plate is bolted permanently to the tube, but as it was to be removed intermittently, there was a slight leakage with any material which was not sufficiently elastic. Silicone grease was both absorbed by the gasket and also dried up with the rise of temperature and became gritty, with the consequent development

of leakage. Silicone rubber gasket was free of these shortcomings. It can be easily cut by using a nail sharpened into a knife-edge and driven half way through a bar of wood, which can be rotated like a compass, with another pointed nail acting as the fixed point. The distance between the two nails should be equal to the diameter of the gasket. Two such devices were used to cut an annular gasket.

To secure a good contact between the gasket and the end of the tube it was hand-ground with emery powder by means of a mild steel grinder specially made for this purpose. The sealing end plate was tightened onto the tube by a clamping fixture studded to the reactor case. The mild steel clamping fixture was made of two supporting studs screwed to the case and a clamping plate, through the middle of which passed a butterfly screw, with a swivel cap on the end. The clamping plate was loosely fixed on one side and free to swing on the other. The free end carried a slot to fit the grooved end of the stud, thus making it possible to tighten or loosen the clamping screw quickly. The swivel plate gave a better grip on the end plate. To guard against the sliding of the reactor tube by the pressure of the clamping screw, it was secured by clamping the permanently sealed end to the case by means of a 1/4" wide, 16 gauge mild steel strip. The air cooling of the open end of the tube was done by blowing compressed air through a copper tube bent into a circle around the silica tube. The circular portion was drilled on the side facing the silica tube with 1/16" drill, making holes at a distance of 3/4 inches. The jets of the air blew through these holes and cooled the portion of the tube outside the reactor.

(3) Insulation:-

Kieselguhr was employed as an efficient lagging material with an apparent density of 27.7 lb/cu.ft. and thermal conductivity of 0.051 B.t.u./((hr.)(sq.ft.)(°F/ft.)) at 204°C. The wires of the heating element passing through it were insulated with clay pipes to save them from chemical action.

(4) Reactor Case:-

The reactor tube and insulation were enclosed in an 18 gauge mild steel case, constructed of two similar and flanged halves which made a hollow cylinder, when screwed together. The circular ends of this cylinder were cut to let the reactor tube fit in them, which was supported on similarly cut circles of Lebah insulation board.

The upper half of the case was slotted for the gas inlet tube and the ends of the Kanthal wire, which constituted the heating element and were insulated from the case by using silica insulation pipes. The case was fastened by means of butterfly screws to the supporting brackets, and suspended on the rack.

(5) Terminal Block:-

The Kanthal wires were connected to the terminal block enclosed in a flanged mild steel box and screwed to the upper half of the case. The terminals were fitted on a mica plate, except the one meant for the earth lead. The

electric cable used was flexible 3 core asbestos covered cotton backed P.V.C. with a 10 Amp current capacity. The current was regulated by a 2 kVA variac.

(6) Temperature Measurement and Control:-

The temperature was measured by Platinum-Platinum + 13% Rhodium thermocouple. The thermocouple wires were covered with thin clay pipes, serving as insulation. The thermocouple block was fitted by means of a rubber bung on the silica sheath. The temperature was measured by an Ether Pyrometer which was a millivoltmeter type temperature indicator for use with Pt-Pt + 13% Rhodium thermocouple with the temperature range 0 - 1500°C. The instrument was fitted with automatic cold junction compensation and had a seven inches mirror-backed scale. The cold junction, situated at the instrument, was adjusted when installed and checked occasionally during use. This was done by disconnecting the leads from the instrument; the pointer should then swing freely around the zero of the instrument. When the pointer settled down, its free position was adjusted by rotating the zero adjustment screw. The temperature at the instrument was set by comparing with a mercury thermometer. The temperature indicator was connected to the terminals on the thermocouple block by means of compensating lead wires. The compensating lead wires were copper-copper + nickel, marketed by Leeds & Northop under the trade name - No. 11 Compensating Lead Wires for Pt - Pt + 13% Rh thermocouples.

(7) Measurements of the Reactor Parts:-**Reactor tube and accessories:-**

Length	I. D.	O. D.
24"	2 $\frac{1}{4}$ "	2 $\frac{3}{4}$ "

Inlet tube:-

Length	I. D.	O. D.
4 $\frac{1}{2}$ "	5/16"	1/2"

Outlet tube:-

Length	I. D.	O. D.
6"	5/16"	1/2"

Thermocouple Sheath:-

Length	I. D.	O. D.
12 $\frac{1}{2}$ "	5/16"	1/2"

Air cooling copper pipe:-

Length of stem	I. D. of tube	I. D. of circular part
10"	1/4"	3 $\frac{1}{2}$ "

Reactor-case:-

Length	Diameter	Width of flange	Thickness
20"	7½"	1"	18 gauge

Terminal box:-

Length	Width	Height	Thickness
12"	3"	2¼"	18 gauge

End Plate:-

Diameter	Thickness	I.D. of groove	O.D. of groove	Depth of groove
3¾"	1"	2¼"	2½"	5/16"

Clamping fixture:-

(1) Studs:-

Length	Thickness	Length of grooved portion	Thickness of grooved portion
4¾"	1/4"	1/2"	3/16"

Distance between the studs

6¼"

(ii) Clamping plate:-

Length	Width	Thickness	Width of slot	Length of slot
7½"	1"	1/4"	3/16"	1/2"

(iii) Clamping screw:-

Length	Thickness	Diameter of swivel plate	Thickness of swivel plate
4½"	1/4"	1"	1/4"

(8) Performance of the reactor A:-

Length of the reactor = 20", diameter = 7½"

$$\begin{aligned}
 \text{Surface area (A)} &= 2\pi r h + 2(\pi r^2) \\
 &= (2 \times \frac{22}{7} \times \frac{15}{48} \times \frac{5}{3}) + 2(\frac{22}{7} \times \frac{225}{2304}) \\
 &= \frac{3300}{1008} + \frac{9900}{16128} = 3.274 + 0.614 \\
 &= 3.888 \text{ sq. ft.}
 \end{aligned}$$

$$Q = hA\Delta T \text{ BTU/hr}$$

where $Q = \text{BTU/hr}$

$h = \text{combined coefficient (7)}$

$A = \text{surface area}$

$T = \text{surface temperature} - \text{ambient temperature}$

Power in resistance loads in AC circuits = $I \times E$

Table 5.3.1.

Performance Data of Reactor A.

Kw		Furnace		Shell		Ambient		Temp. rise		T	Q(Btu/hr)		
Amp	Volts	Kw.	Temperature	Temperature	Temperature	Temperature	Temperature	in	($t_S - t_A$)	h	Kw x 3415	hA ΔT	
				t_S		t_A		Furnace	$(t_S - t_A)$		Btu/hr		
				$^{\circ}C$	$^{\circ}F$	$^{\circ}C$	$^{\circ}F$	$t_F - t_A$	$^{\circ}C$				
1	20	0.02	50	122	21	69.8	21	69.8	29	0	0	68.3	0
2	50	0.10	250	482	43	109.4	21	69.8	229	39.6	1.85	341.5	284.835
3	80	0.24	540	1004	68	154.4	19.5	67.1	520.5	87.3	2.02	819.6	685.633
4	107	0.428	800	1472	102.5	216.5	21.5	70.7	778.5	145.8	2.3	1461.62	1303.802
5	134	0.67	1020	1868	144	291.2	22.5	72.5	997.5	218.7	2.65	2288.05	2253.31
6	160	0.96	1210	2210	171.5	340.7	17	62.6	1193	278.1	3	3278.4	3243.758
6.7	177	1.186	1320	2408	188	370.4	23.5	74.3	1296.5	296.1	3.1	4050.19	3568.834

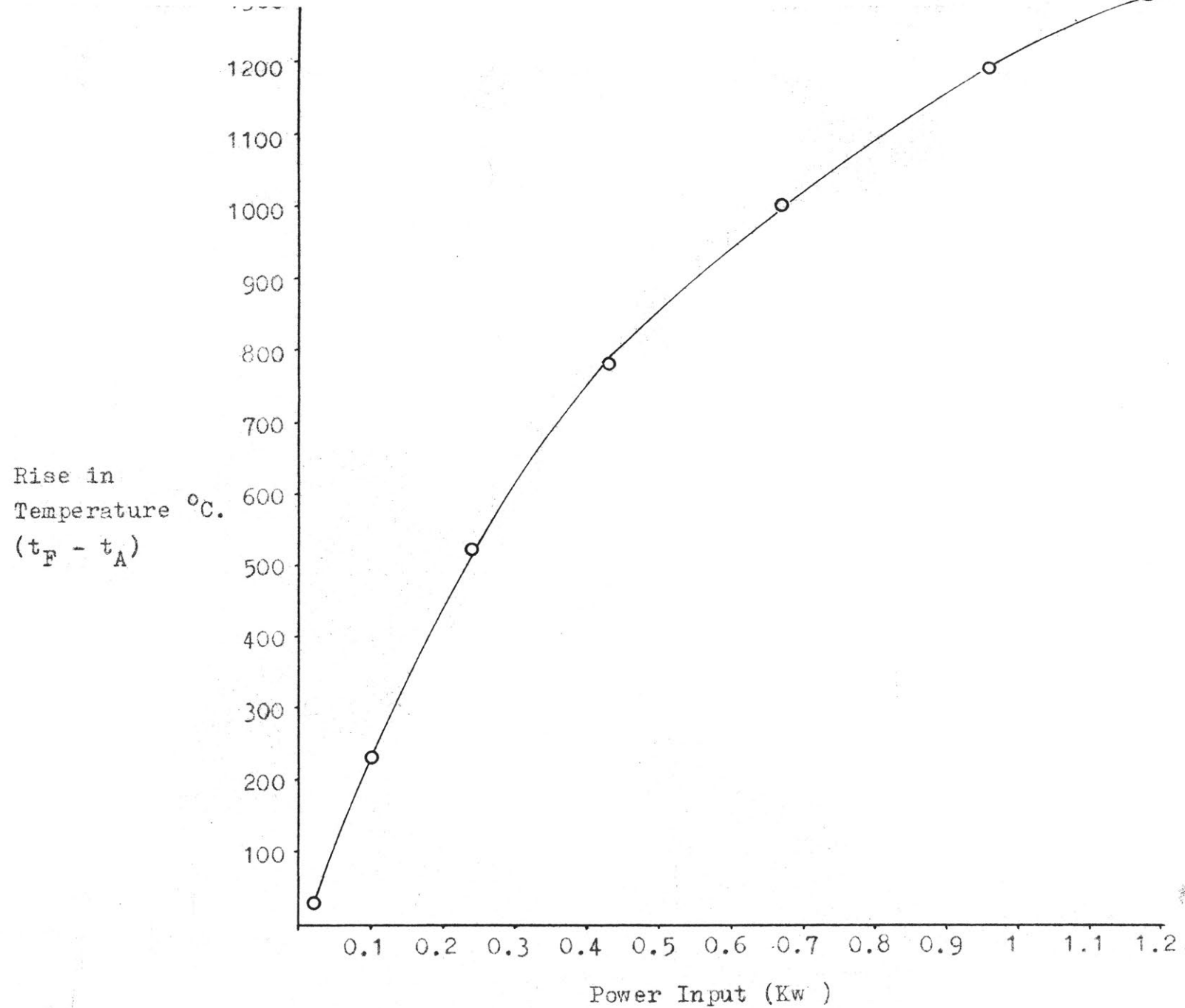


Fig. 5.3.8.

Design of Reactor B (1700°C):-

Introduction:-

The following methods of producing high temperatures were investigated:

- (i) Liquid salt bath furnace.
- (ii) Globar furnace.
- (iii) Carbon resistance furnace.
- (iv) Molybdenum furnace.
- (v) Induction furnace.
- (vi) Wire wound furnace.

Limitations:-

(i) Liquid salt bath furnace -

Three general temperature ranges are available in Houghton's Liquid Salt Baths, viz. 350 - 1000°F.; 1000 - 1900°F. and 1800 - 2350°F. Obviously the desired temperature is not obtained. Fuming of the Bath and size and shape of equipment and time taken to heat up are additional problems.

(ii) Globar furnace -

The Globar rod type AT furnaces are also employed for high temperature work. The resistance of a rod is approximately 1.8 ohms, which decreases with usage, hence the need for high amperage and step down transformers. The globar rods are mechanically weak and when one rod ceases

to work the companion rods have also to be renewed. The price of a rod being nearly £10 each, the furnace becomes costly to operate. The additional disadvantages are the high current cost and the price of transformer.

(iii) Carbon resistance furnace -

These furnaces are heated either by packed carbon granules or by tubular carbon elements. Their operating cost is high due to high current consumption and are liable to burn up due to the oxidation of heating elements, hence the desirability of operating them in vacuum. Thus the cost of vacuum equipment is an additional deterrent in setting up such a furnace.

(iv) Molybdenum wound furnace -

At temperatures above 600°C , molybdenum forms a volatile oxide, hence the need for the protection of winding by placing it in an atmosphere of N_2 and H_2 . The purging atmosphere can be supplied from a cylinder of liquid ammonia, the gas being cracked on steel wool in an ancilliary furnace at about 800°C . So long as a pressure slightly greater than the atmospheric is maintained in the casing, there can be no risk of explosion.

(v) Induction furnace -

In such a furnace metallic materials placed in a water-cooled copper coil can be heated by high frequencies, with the formation of eddy currents. The defects are the

non-uniform heating, high power loss, control difficulties and the problem of heating non-metallic or non-carbon materials. This method of heating is costly and unsuitable for the project in hand.

Advantages of a wire wound furnace:-

For the control of temperature and the rate of change of temperature, an electric furnace is ideal. The electric furnace has another advantage: it is possible to construct furnaces for special purposes to work in restricted spaces or under conditions, where no other means of heating is practicable.

Design Considerations of Reactor B:-

It was decided to heat reactor B with Platinum Rhodium winding. The 20% Rhodium alloy has a high melting point (1750°C) and great resistance to oxidation, it is thus a useful material for furnace windings. Of economic necessity the windings usually used were thinner than would otherwise be used, but it should not be forgotten that much of the cost may be recovered when the winding fails by returning it to the manufacturer. Usually 10% Rhodium alloy is used, but it was decided to use 20% alloy for high specific resistance and improved strength when hot. It is also less ductile than pure platinum. It is best to keep the wire hot and to avoid mechanical abuse at all times, such as is involved in fast heating and cooling.

The following were the design details of the parts:-

(1) Heating element:-

Diameter of the Platinum -20% Rhodium wire = 0.02"

For resistance loads in A.C. circuits $R = \frac{V}{A}$

From a 2 kVA variac, the current which can be drawn at 240 volts = $\frac{2000}{240} = 8.33$ amps.

$$\therefore R = \frac{240}{8.33} = 28.81 \text{ ohms.}$$

The specific resistance of alloy = 20 microhms/cm³ at 20°C

The resistance of alloy per yard at 20°C = 0.88 ohms.

The resistance of alloy per yard at 1500°C = 2.59 ohms.

Thus allowing for approximately 3 times the increase of resistance at working temperatures, the length of the wire required = $\frac{28.81}{0.88 \times 3} = 10.9$ yards approximately.

32 feet of 0.02" thick wire were obtained and wound on a 1½" O.D. mullite tube. Ten turns per inch were employed giving a total of 9½" long element and the winding was anchored at each end to loops of Pt-Rhodium wire, made out of 5 inch long pieces cut from the same wire. Before winding an asbestos sheet was wrapped around the tube, on which the points were marked showing the positions of turns. The wire had to be protected from the influence of sodium or silica. It must not be brought into contact with silica under

reducing conditions at high temperatures, as platinum silicate may be formed. Neither must carbonaceous gas touch it. The element was coated with Triangle R 909 cement supplied by Morgan Crucible Company. This is a setting cement and can be used up to 1900°C .

(2) Reactor tube and accessories:-

The requirements from the reactor tube operating at temperatures close to 1700°C are very exacting. Many tubes at these temperatures bend or crack. Some are not impervious. After comparing all brands available in the market Triangle H.5 Mullite tube, marketed by Morgan Crucible Co., was selected. It is an improved porcelain with a high mullite content, very refractory and providing impermeability at temperatures up to 1700°C . The micro-crystalline mullite structure ensures very high resistance to chemical attack, has a high mechanical strength, and a wide margin of resistance to cracking under temperature gradient.

The reactor tube was sealed on each end by stainless steel adapter and plates which were hollow cylindrical in shape, with the outwardly protruding collars around the holes. On the inlet side the end plate had a collared hole in the centre to provide for a glass tube bringing in gases, to produce any desired atmosphere in the reactor. It can be tightened on the tube by means of a clamping fixture, bolted to split collar clamps fixed on the mullite tube to avoid the build up of pressure on the hot portion of the tube, as would happen if the clamping fixture is bolted to the reactor case. The clamping butterfly screw of the fixture had a yoke at the end to provide space for the right angled glass

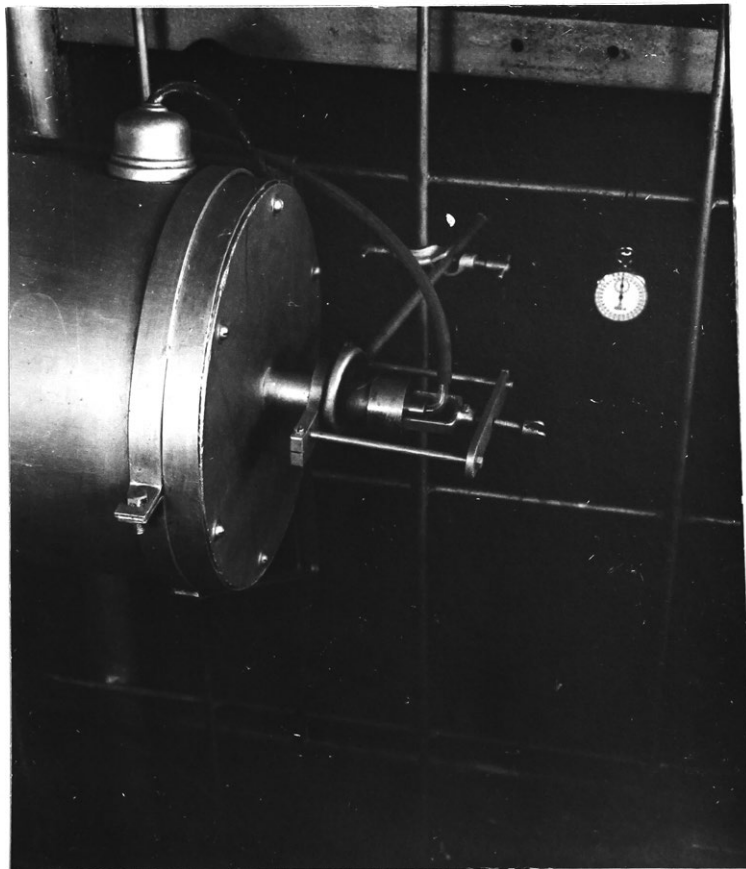


Fig. 5.3.9
Inlet side of Reactor B.

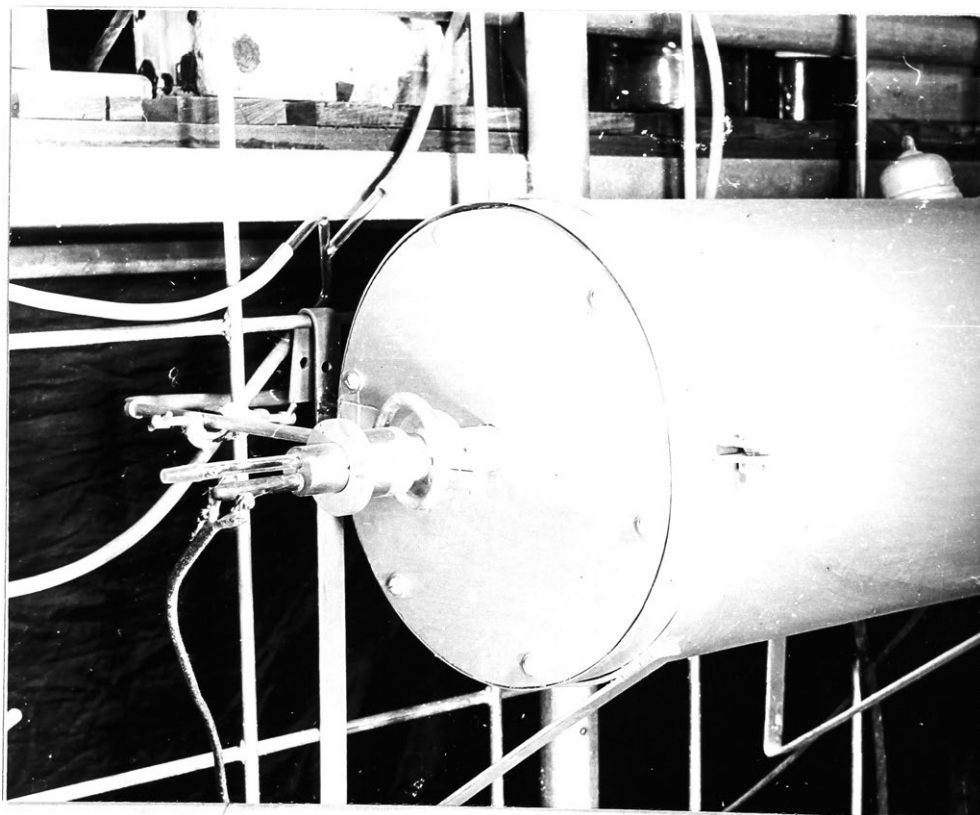


Fig. 5.3.10
Outlet side of Reactor B.

tube leading into the collared hole of the adaptor end plate. The clamping plate was similarly constructed as the one used in the clamping fixture of reactor A and can be swung on or off, quickly for tightening purposes.

The adaptor end plate on the outlet side of the reactor tube had two collared holes to provide for the mullite thermocouple sheath and a B10 glass cone to serve as an outlet for the gases. This end plate was shouldered to provide space for a mild steel ring collar, which in turn was bolted to split collar clamp. Both split collar clamps were fixed on the mullite tube with a pad of asbestos tape in between.

The adaptor end plates contained silicone rubber gaskets cut by the sharp edged/^{steel}tubes of appropriate size, having appropriately sized holes for the passage of tubes and thermocouple sheath. To avoid any leakage each gasket was made of 3 circles of silicone rubber joined to one another by silastic 110 adhesive, sold by Dow Corning Corporation of Michigan U.S.A. To safeguard against the effect of high temperature on gaskets by conduction, air cooling of both ends of reactor tube was done by blowing air jets through the holes drilled in a copper tube bent into a circle around the reactor tube, as described earlier.

Platinum radiation shields:--

To guard against the burning of the gaskets by radiation, platinum radiation shields were employed on each end. They consisted of discs of platinum. The shield on the

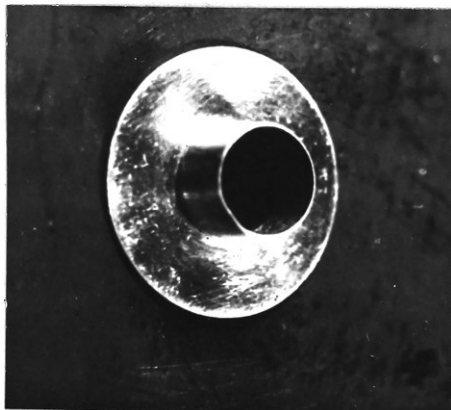


Fig. 5.3.11
Radiation Shield on the Inlet Side.



Fig. 5.3.12
Radiation Shield on the Outlet Side.

inlet side had one collared hole in the centre and slides on the glass tube meant for inlet gases. On the outlet side the shield had two holes, one was collared and meant for the passage of thermocouple sheath through it and the other one served as the exit for the gases and was shielded on the gasket side by means of a platinum strip bent at right angles in the middle and soldered to the disc. This shield rested on the thermocouple sheath near the end of the hot portion of the reactor tube.

(3) Insulation:-

The reactor tube was enclosed in a silica tube of 2 $\frac{1}{4}$ " O.D. and filled with alumina which acted as insulation. The ends of the element wires passed through a hole drilled in the silica tube and connected to the terminal box fixed on the reactor case. The wires were insulated from the case and each other by double holed ceramic pipe which also afforded protection from any harmful substance in the insulation material. The space between the silica tube and the reactor case was filled with kieselguhr.

(4) Reactor case:-

The reactor case was made of 18 gauge mild steel and was cylindrical in shape. The ends of the cylinder were closed by screwing together two circular pieces of $\frac{1}{4}$ " thick Sindanyo insulation board and fitting to the case by means of lugs. The pieces on the inner side had circular holes in the centre to support the ends of the silica tube and the pieces on the outside had holes for the reactor tube, which was stopped from rotating in the reactor by clamping it on both sides and inserting the arms of the clamp in slots, carved on the inside of the outer Sindanyo boards.

The reactor case was suspended on the rack by means of supporting brackets.

(5) Terminal block:-

The terminal block was made of ceramic through which a 3rd hole was drilled for the earth terminal, screwed to the metallic case. The electric cable used was flexible 3 core, asbestos covered, cotton backed P.V.C., with a ten amp. current capacity. The current was regulated by a continuous duty 2 kVA autotransformer, with thicker windings.

(6) Temperature measurement and control:-

The temperature was measured by Platinum-Platinum 13% rhodium thermocouple enclosed by the mullite thermocouple sheath and reaching up to the centre of the hot portion of the reactor tube. Due to the lack of space the thermocouple block had to be made with exact requirements. It consisted of a cylindrical piece of hard wood with 0.02 inches diameter twin holes, coming out in the middle, on opposite sides. The ends of the thermocouple wires coming out through them were connected to two screw type terminals fixed near each hole, and the e.m.f. generated was taken through the compensating leads already mentioned to the temperature indicator, which has also been described earlier. For measuring temperatures higher than 1500°C, a potentiometer was used.

(7) Measurements of the reactor parts:-

Reactor tube:-

Length	I.D.	O.D.
30"	7/8"	1 1/4"

Inlet tube:-

Length	I.D.	O.D.
3 1/2"	7/32"	5/16"

Outlet tube:-

Length	I.D.	O.D.
5½"	7/32"	5/16"

Thermocouple sheath:-

Length	I.D.	O.D.
16"	9/32"	12/32"

Platinum Radiation shields:-

(i) Radiation shield on the inlet side:-

Diameter of disc	Thickness of disc & collar	Diameter of hole	Length of collar
7/8"	0.02"	11/32"	1/4"

(ii) Radiation shield on the outlet side:-

Diameter of disc	Diameter of hole for the thermocouple sheath	Length of collar
7/8"	$\frac{25}{64}$	1/4"

Thickness of disc,
collar and strip
0.02"

Diameter of hole for
the exit of gases
11/32"

Dimensions of strip

$$\frac{22}{32} \times \frac{13}{32}$$

Air cooling copper pipes:-

Length of stem	I.D. of tube	I.D. of circular parts
10"	1/4"	2"

Case:-

Length	Diameter	Thickness
23"	1 ft.	18 gauge

Adaptor end plates and Accessories:-

(a) Inlet side:-

Length of the hollow cylindrical portion	1-3/8"
O.D. " " " " "	1-5/8"
I.D. " " " " "	1-3/8"
Diameter of the hole for thermocouple sheath	7/16"
Diameter of the hole for outlet tube	3/8"
Length of the collar around the holes	1 1/4"
O.D. of collar	1-1/8"

Retaining ring:-

O.D.	I.D.	Thickness
2 1/4"	1-3/16"	1/4"

Studs:-

Length	Thickness	Distance between both studs
3 1/2"	3/16"	2"

Split collar clamp:-

Length	O.D.	I.D.	Thickness
3 1/2"	2 1/4"	1 1/2"	3/8"

(b) Outlet Side:-

Length of the cylindrical portion	7/8"
O.D. " " " "	1-5/8"
I.D. " " " "	1-3/8"
Diameter of hole	3/8"
Length of collar around the hole	1/2"
O.D. of collar	5/8"

Clamping Fixture:-

(1) Studs:-

Length	Thickness	Length of grooved portion	Thickness of grooved portion
5 1/2"	1/4"	1/2"	3/16"

Distance between studs

4 1/2"

(ii) Clamping plate:-

Length	Width	Thickness	Width of slot	Length of slot
5 1/2"	1"	1/4"	1/4"	1/2"

(iii) Clamping screw:-

Length of screw	Thickness of screw	Length of yoke	Width of yoke	Thickness of yoke
4"	1/4"	2"	1 1/4"	3/32"

(iv) Split collar clamp:-

O.D.	I.D.	Length	Thickness
2 1/4"	1 1/4"	6"	3/8"

(8) Performance of the Reactor B:-

Length of case = 23"

Diameter " = 12"

$$\text{Surface area} = 2\pi rh + 2(\pi r^2) = (2 \times \frac{22}{7} \times \frac{1}{2} \times \frac{23}{12}) + 2(\frac{22}{7} \times \frac{1}{4})$$

$$= \frac{1012}{168} + \frac{44}{28} = 6.024 + 1.571$$

$$= 7.595 \text{ sq. ft.}$$

Resistance of 31 ft. of Pt-20% Rhodium wire (1 ft. has been subtracted, because 10" were used for anchoring and 1 inch is screwed to each terminal) at room temperature = $\frac{0.88 \times 31}{3}$

$$= 9.1 \text{ ohms}$$

Table 5.3.2.

Performance Data of Reactor B.

E.w.			R	Furnace		Shell		Ambient		Temp. rise		h	Q (Btu/hr)	
Amp	Volts	Kw		Temperature		Temperature		Temperature		in	T		Kw x 3415	h ΔT
				t_F		t_S		t_A		Furnace	$(t_S - t_A)$			(Btu/hr)
				$^{\circ}C$	$^{\circ}F$	$^{\circ}C$	$^{\circ}F$	$^{\circ}C$	$^{\circ}F$	$t_F - t_A$	$^{\circ}F$			
										$^{\circ}C$				
1	15	0.015	15	190	374	23	73.4	23	73.4	167	0	0	51.225	0
2	30	0.06	15	420	788	18	64.4	18	64.4	402	0	0	204.9	0
3	66	0.198	22	1122	2051.6	46.5	115.7	25.5	77.9	1096.5	37.8	1.85	676.17	531.128
4	110	0.44	27.5	1566	2850.8	68	154.4	23	73.4	1543	81.0	2	1502.6	1230.39
4.5	125	0.5625	27.8	1700	3092	81.5	178.7	23	73.4	1677	105.3	2.1	1920.938	1679.482

Characteristics of Reactor B.
Rise in Furnace Temperature Vs Power Input.

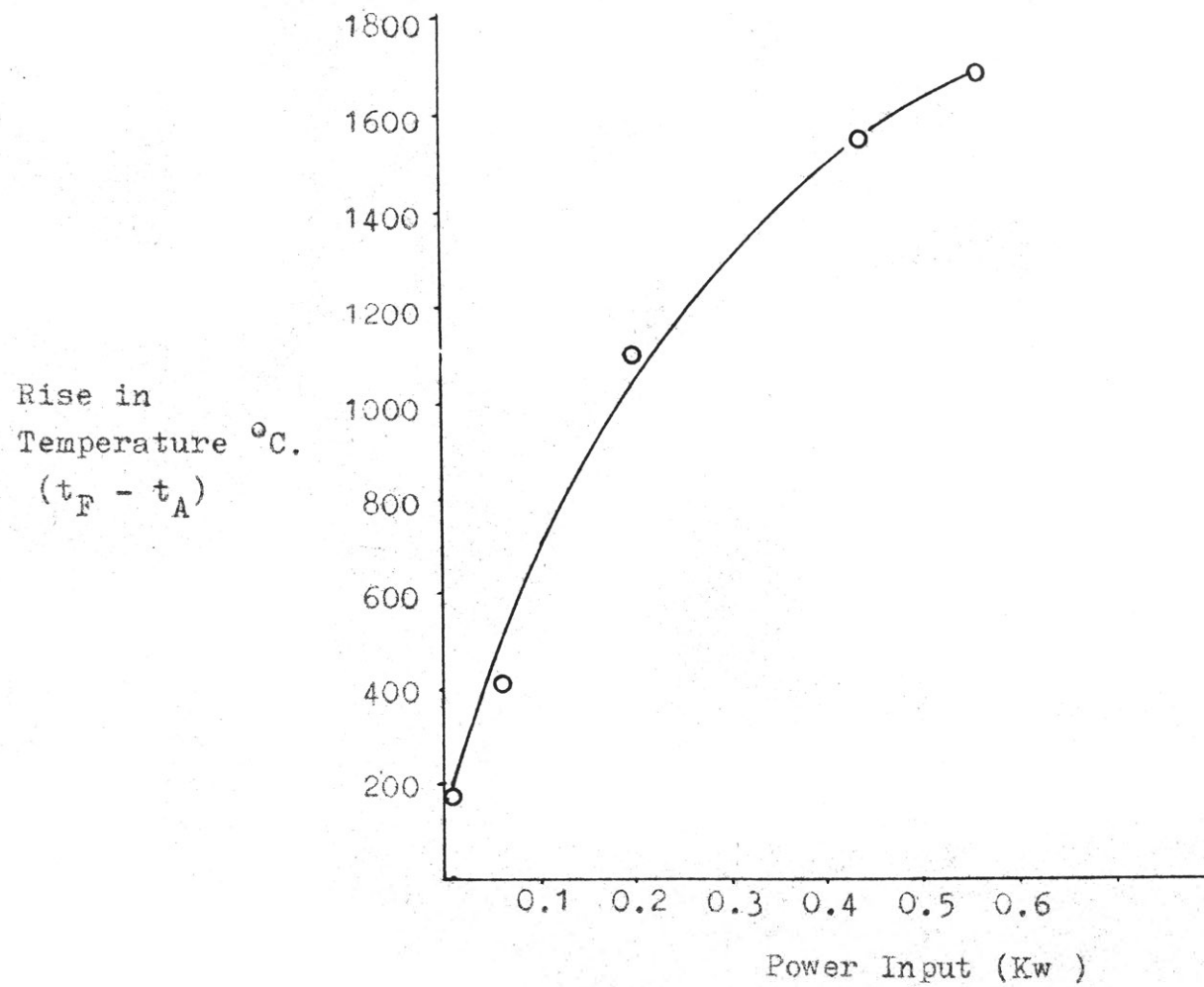


Fig. 5.3.13.

Characteristics of Reactor B.

R Vs Power Input.

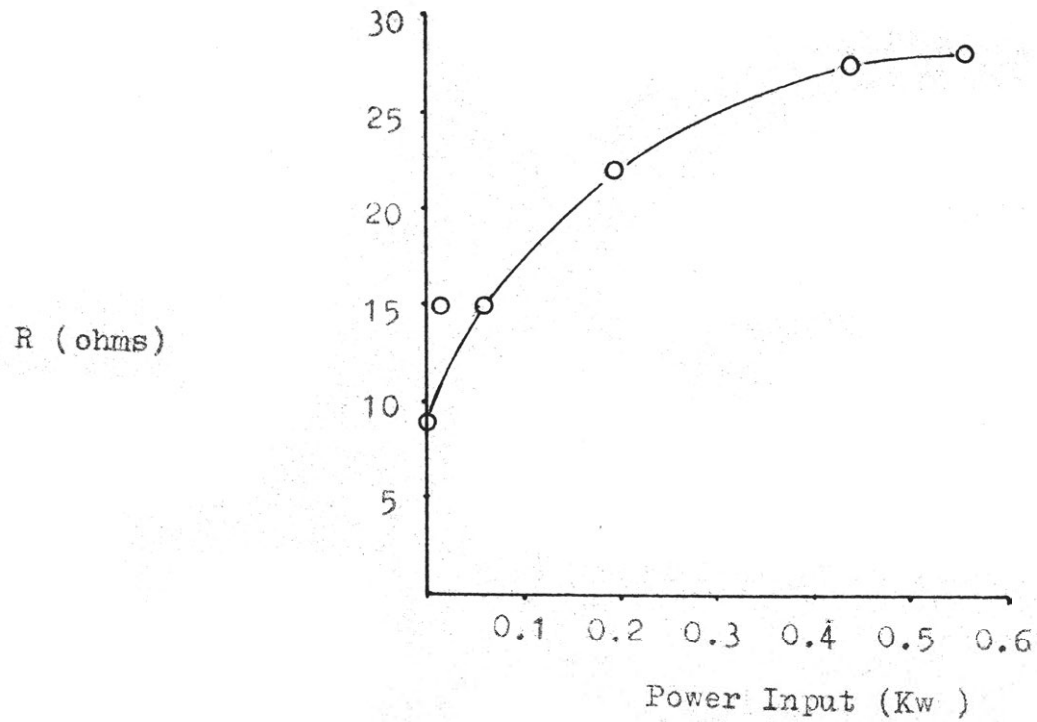


Fig. 5.3.14.

IV. Studies in the Absorption of Oxides of Sulfur:-

It was decided to absorb the oxides of sulfur in hydrogen peroxide for conversion to sulphuric acid, which in turn gave rise to the problem of designing an efficient gas absorber. Two types of absorbers were made to study this question:-

(A) Sintered disc type absorbers.

(B) Spiral type absorbers.

Description of each type is as follows:-

(A) Sintered Disc type Absorbers:-

Jena frit glass discs of the grades G0, G1, G2, G3 and G4 were purchased and Dreschel type absorbers were made. Whereas the size of bubbles obtained from G0 discs was large and size G2, G3 and G4 gave small bubbles, it was noted that the build-up of gas pressures in the system, with size G2, G3 and G4 disc absorbers was high. G1 disc absorber gave the appropriate sized bubbles with the pressure development of 20-5/8 inches of water.

During the study of bubble formation it was seen, that the bubbles typical of the frit glass discs of each grade were formed only if the discs faced upward. With inverted discs only a single large bubble was obtained at a time. On the other hand if the discs were to face upwards and the gas inlet tube was joined to it on the side, too much space was required, which in turn meant large volumes of

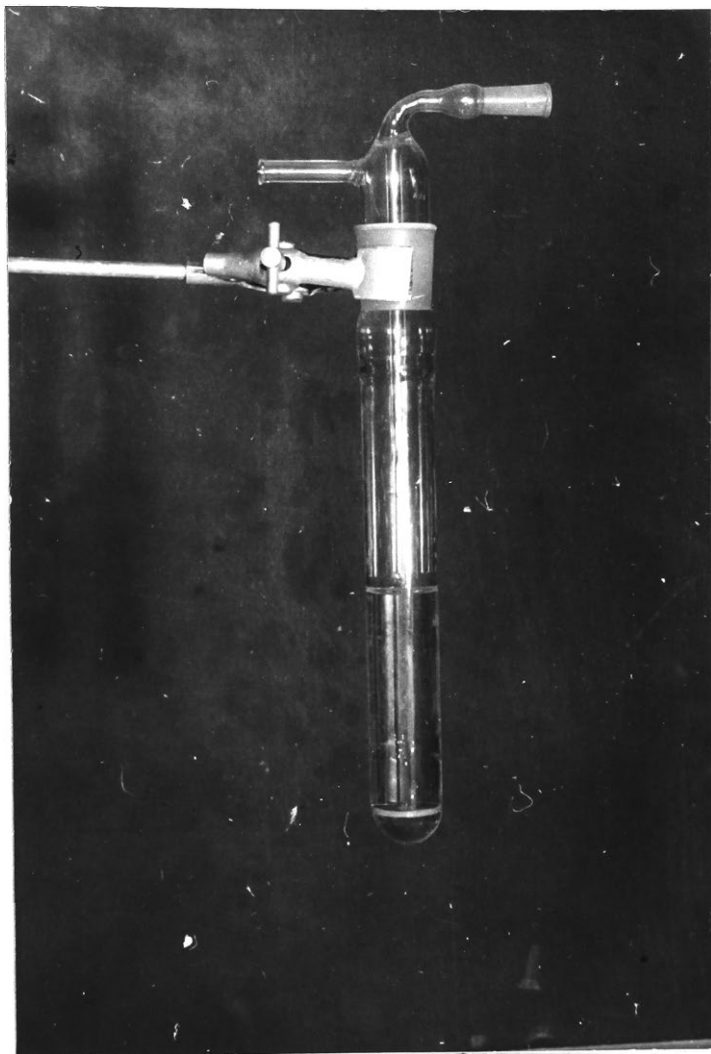


Fig. 5.4.15
Sintered Disc Type
Absorber.

absorbing liquid ever to be used to give sufficient head for absorption. To overcome this problem the gas inlet tube was joined, to the disc by boring a hole in its centre.

The measurements of the absorber were as follows:-

Length of absorber	10 inches	
I.D. of absorber	1-1/8 inches	
Size of main joint	B 34	
Length of inlet tube	11 inches	
I.D. of inlet tube	3/16 inch	Size of the inlet tube socket = B10
Diameter of G1 Frit		
glass disc	3/4 inch	
Length of the outlet tube	1 1/2 inches	
I.D. of the outlet tube	1/4 inch	

Although absorber A was very efficient, it was found that due to the build up of pressure in the system, the liquid in the flowmeter was pushed out, by the sudden release of pressure, when the reactor was opened intermittently to take the boats out. It was decided to use this absorber for hydrogen sulphide absorption, in sulphide determinations, where the above mentioned difficulty did not arise.

(B) Spiral type Absorber:-

To eliminate the chance of any leakage of gases from the reactor or interference with flowmeter fluid, due to the build up of pressure, it was necessary to make an efficient absorber, with minimum pressure development. As

the gases to be absorbed were mixed with large amounts of air and oxygen, ordinary gas absorption bottles and tubes were found inefficient. Same was the case with Friedrich moulded spiral type, and beaded type absorbers.

A literature survey was done to study the absorbers designed by Weaver and Edwards (127), Milligan (91), Beaumont, Willaman and De Long (23), Harvey and Regensbal (61), Martin and Green (84) and Martin (83).

Martin's absorber of the following dimensions was made:-

Height of apparatus, cm	60	Spiral tube:	
Reservoir:		Length, cm.	180
Height, cm.	11	Diameter, cm	0.6
Diameter, cm	8	Inlet Jet:	
Capacity, ml	300	Diameter of	
Vertical tube:		lead in tube, cm	0.4 -
Length, cm	42		0.5
Diameter, cm	0.6	Diameter of orifice, cm.	
			= 0.05

Martin's absorber was primarily designed for the absorption of CO_2 . It was found to have the following drawbacks:-

- (a) It developed a pressure of 19 inches of water in the system.
- (b) Due to the length and extension of the spiral tube, the gases escaped through the vertical tube instead of the spiral as soon as the reactor was sealed.



Fig. 5.4.16
Martin's Absorber.

- (c) The diameter of the orifice was too small.

Features of the designed spiral type SO_2 absorber:-

To overcome the above mentioned difficulties studies were made as follows:-

- (a) Coils were made from tubes of various lengths and varying distances between each turn of the coil. It was found that a close wound coil made from 90 cm long and 0.6 cm internal diameter tube gave good absorptions as well as reduced the pressure considerably.
- (b) In order to eliminate the escape of gases through the vertical tube instead of the spiral, the length of the U shaped portion of the tube joining the spiral with the vertical tube was increased.
- (c) The reservoir was made cylindrical in shape to facilitate titration work and provide an opening for the stirrer, if the additional stirring is found necessary. The absorber could be easily corked at the top and the gases could be taken through the outlet tube to another absorber.
- (d) The diameter of orifice was increased to 1 mm.

The dimensions of the absorber were as follows:-

Height of apparatus, cm	45
cylindrical tube:	
length, cm.	17.5
diameter, cm.	5

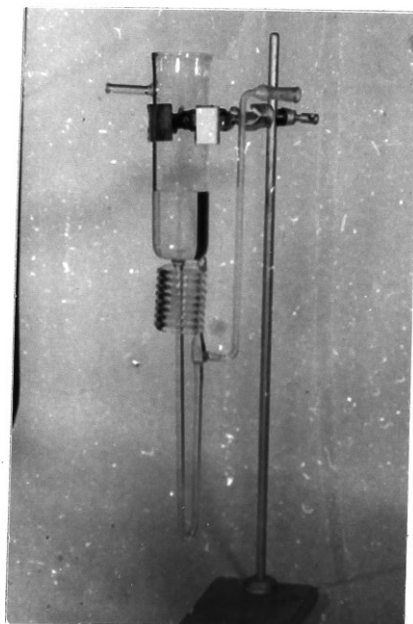


Fig. 5.4.17
Designed Spiral Absorber.

Capacity ml	200
Vertical Tube:	
Length, cm	27.5
Diameter, cm	0.6
Spiral tube:	
Length, cm	90
Diameter cm	0.6
Inlet Jet:	
Dia. of lead in	
tubes, cm	0.4 - 0.5
Dia. of orifice	
cm	0.1

The diameter of the orifice was measured by an inspectscope magnifier which has an inbuilt graticule. The designed absorber was thus a quantitative absorption vessel in which the absorbing solution was titrated directly, thus obviating the errors which inevitably occur, when aliquots are removed for titration. The gases were passed through the apparatus charged with neutral H_2O_2 solution, which was then titrated within the equipment. Either compression or suction may be used to move the gases through the system.

The principal advantages of the above absorber over most of those in general use were its efficiency in absorption, its small capacity for absorbing solution, and its design, which permitted direct titration. Inasmuch as it will operate on as little as 30 ml of liquid, relatively concentrated absorbing solutions could be used without requiring inconveniently large volumes of standard solution in titration. It reduced the pressure in the

system to 5-11/16 inches only.

A comparative study of pressure development in the system for absorbers containing 100 cc of H_2O_2 solution each, is given in table 5.4.3.

Table 5.4.3.

Comparative Study of Pressure Development
Due to Absorbers.

Rate of Aspiration	Designed spiral absorber (inches of water)		Designed sintered disc absorber (inches of water)		Martin's Absorber (inches of water)	
	Before bubbles start	During bubbling	Before bubbles start	During bubbling	Before bubbles start	During bubbling
100 cc/ min	6 $\frac{3}{4}$	5-11/16	21	20-5/8	19	15
150 cc/ min	7-3/8	5 $\frac{3}{4}$	21-1/8	20-7/8	21 $\frac{1}{2}$	15-1/8
180 cc/ min	7-7/8	5-7/8	21 $\frac{1}{2}$	21-1/8	23 $\frac{1}{2}$	15 $\frac{1}{2}$

Comparison of absorber efficiencies:-

The efficiency of each of the absorbers was

determined by passing through it a current of carbon dioxide free air at various rates into which was liberated a known amount of sulfur dioxide. This was accomplished by slowly dropping standard sodium sulphite solution from a burette, into a closed conical flask containing hydrochloric acid. The orifice of burette was adjusted to deliver 200 cc of solution/hour. To eliminate the risk of absorption of sulfur dioxide in HCl, it was kept boiling. As very brisk boiling blocked the outlet tube due to condensation of water, resulting in irregular flow of gas mixture, a double walled condenser with a wide inner tube was interposed between the gas generator and the absorber. In addition boiling water was used to heat the flask containing HCl, making it boil evenly. These precautions were necessary for controlling the flow accurately.

As the evolution of SO_2 was slow, the gas was swept by air flow to the absorber containing H_2O_2 solution. An additional absorber was connected in series to the first absorber. When the first absorber had absorbed maximum amount of SO_2 , the excess was carried over to the second absorber, changing the colour of the indicator in it immediately.

From the amounts of SO_2 absorbed, the equivalent amount of CaSO_4 , which will evolve the same amount of SO_2 on desulfurisation can be calculated.

The results are summarised in table 5.4.4.

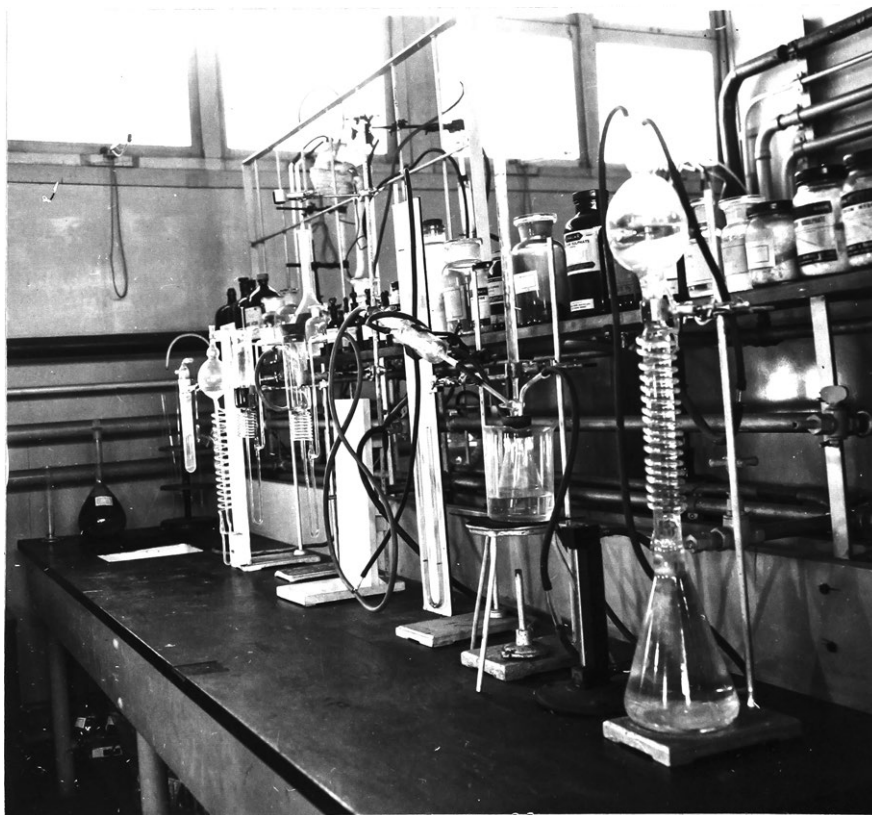


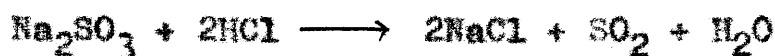
Fig. 5.4.18
Equipment for the Comparison of
Absorber Efficiencies.

Calculations:-

63.03 gm/litre solution of Sodium sulphite was prepared.

1 ml of this solution = 0.06303 gm Na_2SO_3

Reaction with HCl produces SO_2 according to the following equation:-



Thus 126.06 gm Na_2SO_3 evolve = 64.06 gm SO_2
 = 32.06 gm S

32.06 gm of S is contained in 136.146 gm of CaSO_4 which will evolve as SO_2 on desulfurisation of CaSO_4

∴ 126.06 gm of Na_2SO_3 is equivalent to 136.146 gm CaSO_4
 ∴ 0.06303 " " " " to $\frac{136.146}{126.06} \times 0.06303$ gm CaSO_4
 = 0.062 gm CaSO_4

Table 5.4.4.

Efficiencies of Absorbers.

Strength of H_2O_2	Rate of Aspira- tion cc	CC N_2SO_3 Solution absorbed (A)		Max: amount of $CaSO_4$ which can be disul- furised $A \times 0.068$ gms.	
		Spiral absorber	Sintered disc no.1 absorber	Spiral absorber	Sintered disc no.1 absorber
10 N	100	243	242	16.524	16.456
10 N	180	229.7	227.2	15.62	15.45
1 N	100	63	60	4.284	4.08

From the data on absorbers, it was decided to use 100 cc of 10 N H_2O_2 in absorbers, in which the gases were passed at a rate of 100 cc/minute. Air and oxygen mixed in the ratio of 10 : 1 were used for sweeping purposes.

V. Equipment for the Estimation of Sulphide:-

As sulphide was estimated by evolving H_2S and absorbing it in ammoniacal zinc sulphate solution, both a generator and an absorber was required. The frit glass disc absorber previously described was used as an absorber. The glass generator had an inlet tube for bringing in an inert gas to act as sweeper and a thistle funnel for adding the acid. The outlet tube had a B10 quickfit cone which could be directly fitted to the socket of the absorber, thus avoiding any rubber connections.

The dimensions of the generator were as follows:-

Height of generator	12½ inches
Generator tube:	
Length	7½ inches
Diameter	1½ inch
Joint	B 34
Inlet arm:	
Length	2 inches
Diameter	5/32 inches
Inlet and acid dropping tubes:	
Length inside the generator	7½ inches
Diameter	5/32 inches
Outlet tube:	
Length	2½ inches
Diameter	5/32 inches
Cone	B10

Oxygen free nitrogen was used as an inert gas and was passed at a rate of 100 cc/min.

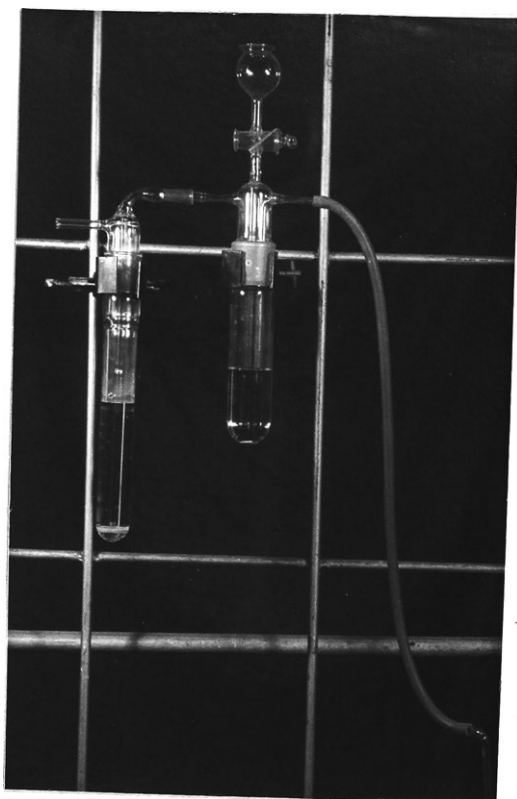


Fig. 5.5.19
 H_2S generator and absorber.

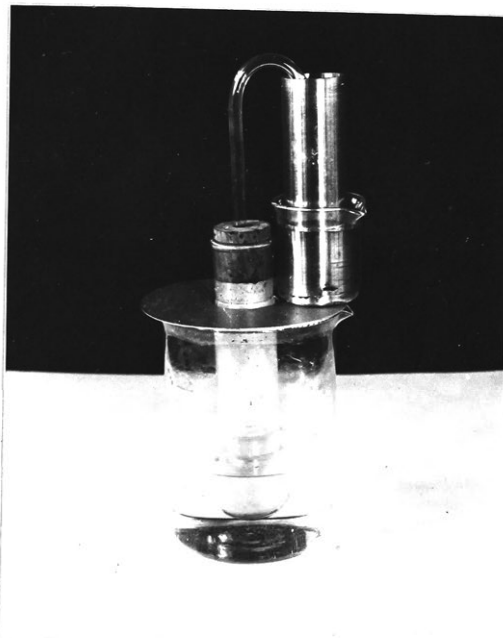


Fig. 5.6.20
Clinker quenching equipment.

VI. Quenching Equipment for Cement Clinker:-

The determination of phases by this method depends upon the fact that instantaneous cooling of the silicate melts, preserves in the charge, the phases present at the temperature, from which the charge was quenched.

As the tricalcium silicate in clinker developes hydrates if cooled in water (27), liquid air was used for quenching. The equipment was simple and effective. It consisted of a 5" x 1½" stainless steel tube placed in a beaker containing liquid air. The pellet along with the boat was dropped instantaneously into the cool tube and was further cooled simultaneously by a strong blast of liquid air, vaporised from a tube, by dipping it in water. This method eliminated spurtng, caused by quenching directly in liquid air, and gave good crystals in the quenched clinker.

VII. Sulfur Condenser:-

It was built on the principle of a rail-road tube and was made of light weight glass components, so that the small weight of sulfur deposited on it could be detectable. The dimensions were as follows:-

Height of absorber	7 inches
Jacket tube:	
Length	6 inches
Diameter	1/2 inch
Cone	B10
Length of Cone Arm	1½ inches

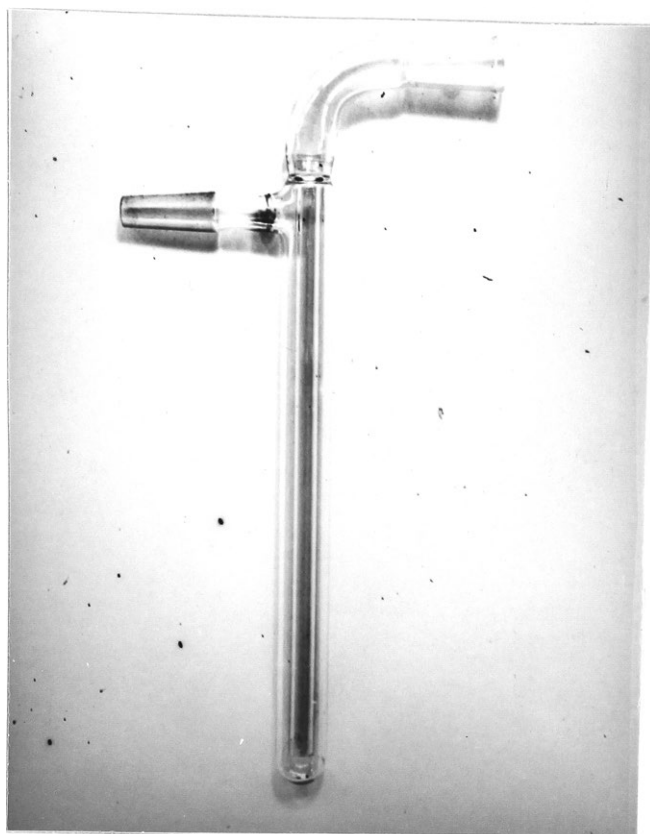


Fig. 3.7.21
Ball Head tube for condensing
sulphur.

Inlet tube:

Length of Jacketed Portion	5 $\frac{3}{4}$ inches
Diameter	1/4 inch
Socket	B10
Length of Socket Arm	1 $\frac{3}{4}$ inches

CHAPTER VI.

SOURCES, PREPARATION AND ANALYSIS OF MATERIALS.

I. Sources:-

Chemicals:- All chemicals used in research were of the purest grade available. Hydrated calcium sulphate, Fe_2O_3 , Al_2O_3 and SiO_2 , the basic components of the systems, were critically examined before use. Precipitated Fe_2O_3 was used and Al_2O_3 was of the quality, used in chromatographic analysis.

Gypsum and Coal:- Gypsum and high sulfur coal were supplied by the Pakistan Industrial Development Corporation procured through the Superintendent Collieries Mari Indus West Pakistan and stored in four gallon tins with lever lids.

II. Preparations:-

Preparation of Pure Carbon:- Pure carbon was prepared by making sugar charcoal and heating it in a furnace at 1000°C , in an inert atmosphere. Nitrogen was used for this purpose. When the volatiles were driven off, the carbon obtained was cooled within the furnace, tested for impurities and bottled.

Preparation of Coke:- Coke was prepared from high sulphur coal, through the courtesy of the Coal Research Station,

C. S. I. R. O., North Ryde. Coking was done in an 18" retort, of eight pounds capacity. This carbonising plant is B.M. - AGA type (103).

Grinding of Samples:- Coal, coke and gypsum were ground in a porcelain ball mill to -200 mesh. Other chemicals employed as components of the systems were also sieved to the same size. A brush was used as a sieving aid for gypsum, which otherwise refuses to pass through, due to the aggregation of particles with hygroscopic moisture. Coal required considerable time for grinding.

Preparation of Coal Ash:- The ash was prepared according to the standard method (46) as follows:-

1. Accurately weigh 1 to 1.01 g of coal of known moisture content (prepared for analysis according to the method given in Fuel Research survey Paper No. 44) in a silica dish (5 cm x 1 cm). Place in a muffle furnace at room temperature and raise the temperature to $490^{\circ}\text{C} \pm 25^{\circ}\text{C}$ in 30 minutes. Maintain at this temperature for 30 minutes, and then heat in an oxidising atmosphere at $775^{\circ}\text{C} \pm 25^{\circ}\text{C}$ for 1 hour or until constant in weight.
2. After incineration cover the dish, transfer the covered dish to a desiccator and allow to cool. Weigh. Brush out the ash and weigh the empty dish.

3. Repeat the determination until a sufficient quantity 0.5 g of ash has been prepared.

III. (A) Analysis of Coal and Coke:-

Coal and coke was analysed on air dried and D.A.F. basis at C. S. I. R. Coal Research Station, North Ryde. 3930 grams of coal were carbonised at 800°C. The yield was 2340 grams of char. The results of analysis are reported in Appendix I.

(B) Analysis of Gypsum and Coal Ash:-

(i) Determination of Free and Combined Water in Gypsum:-

Procedure:- (III)

(a) Free Water:- The sample spread out in a thin layer is weighed in a basin and dried in an oven for 2 hours at 45°. It is then cooled in a desiccator and weighed again. The loss of weight corresponds to free water and is calculated to percentage of sample as received.

(b) Combined Water:- Place 1 gm of the sample in a covered crucible and dry at 215 to 230°C to constant weight. Calculate the loss of weight to percentage of sample as received and report as combined water.

Calculations:-

(a) Free Water:-

Weight of basin = 31.0951 gm

Weight of basin + gypsum = 56.3253 gm

∴ weight of gypsum taken = 25.2302 gm

weight of basin + gypsum after removal
of moisture = 56.3065 gms.

∴ weight of dry gypsum = 25.2114 gms.

∴ moisture = $0.0188 \times \frac{100}{25.2114}$
= 0.0746%

(b) Combined Water:-

Weight of beaker = 24.1266 gm

weight of beaker + gypsum = 25.1260 gm

∴ weight of moist gypsum taken = 0.9914 gm

∴ weight of dry gypsum taken = $0.9914 \times \frac{99.93}{100}$

= 0.9907 gm

weight of beaker + gypsum after $2H_2O$
removal = 24.9105 gm

∴ $CaSO_4$ in gypsum = 0.7839 gm

∴ Combined water = $\frac{0.2068}{0.9907} \times 100$

= 20.874%

(ii) Determination of Sulphate Contents of Gypsum and Coal Ash:-

Procedure:-

(a) Gypsum:- Dissolve 0.5 gm of the sample in 50 ml of 1:5 HCl. Boil. Add 100 ml of boiling water and continue

boiling for 5 minutes. Filter immediately and wash thoroughly with hot water. Boil, and while boiling add slowly 20 ml of a boiling 10% solution of BaCl_2 . Digest hot for 1 hour or until precipitate settles. Filter and wash. Dry carefully. Ignite over Bunsen burner at lowest heat possible until filter paper is burned off. Ignite at bright red heat for 15 minutes and weigh. Multiply this weight by 0.13735 to determine the weight of S. Then calculate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to percentage of sample as received.

(b) Coal Ash:- Treat a separate portion of 0.5 g of the ash with 100 cc of HCl and 5 cc of bromine water and allow to digest at boiling point for 1 hour. Filter the liquid through a gravimetric filter paper and wash the insoluble residue with hot water. Cover the residue. Boil the filtrate and while boiling treat with 15 cc of 10% BaCl_2 solution added drop by drop to permit of uninterrupted boiling. Boil the liquid to a further 15 minutes and then allow to stand for at least 2 hours or overnight if the percentage of sulphur is small. Filter on fine paper or in a Gooch crucible, wash with hot water until the washings give not more than a trace of opalescence with AgNO_3 solution. Dry and ignite, oxidising the filter ash in the usual manner with a drop of HNO_3 and sulphuric acids.

Calculations:-

(a) Gypsum:-

(i) Weight of gypsum taken = 0.4874 gm
 weight of ignited crucible = 12.9408 gm
 weight of ignited crucible + BaSO_4 = 13.6003 gm
 weight of filter paper ash = 0.00007 gm
 \therefore weight of BaSO_4 = 0.65943 gm
 \therefore $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ equivalent of BaSO_4 = 0.65943
 $\times 0.13735 \times \frac{172.178}{32.06}$ gm
 = 0.09057 \times 5.3704 gm
 = 0.4864 gm
 \therefore % gypsum = $0.4864 \times \frac{100}{0.4874}$
 = 99.79

(ii) Weight of gypsum taken = 0.4758 gm
 weight of ignited crucible = 16.5051 gm
 weight of ignited crucible + BaSO_4 = 17.1485 gm
 weight of filter paper ash = 0.00007 gm
 \therefore weight of BaSO_4 = 0.64333 gm
 \therefore $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ equivalent of BaSO_4 = 0.64333
 $\times 0.13735 \times \frac{172.178}{32.06}$ gm
 = 0.08836 \times 5.3704 gm
 = 0.4745 gm
 \therefore % gypsum = $0.4745 \times \frac{100}{0.4758}$ = 99.727
 \therefore Mean $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ = 99.758%

(b) Coal Ash:-

Weight of watch glass = 15.2918 gm

weight of watch glass + ash = 15.5633 gm

∴ weight of ash taken = 0.2715 gm

weight of ignited crucible = 12.9420 gm

weight of ignited crucible + BaSO_4 = 12.9500 gm.

weight of filter paper ash = 0.00007 gm

∴ weight of BaSO_4 = 0.0080 gm

∴ SO_3 equivalent of BaSO_4 = 0.008×0.13735
 $\times \frac{80.06}{32.06}$ gm

= 0.00274 gm

% SO_3 = $\frac{0.00274 \times 100}{0.2715}$
 = 1.011%

CaSO_4 equivalent of BaSO_4 = $0.008 \times 0.13735 \times \frac{136.146}{32.06}$ gm

= 0.004666 gm

∴ % CaSO_4 = $0.004666 \times \frac{100}{0.2715}$

= 1.7186%

(iii) Determination of Fe_2O_3 content of Coal Ash and Gypsum:-

(a) Preparation of Solution of Coal Ash:-

1. Accurately weigh 0.2 gm of ash in a platinum crucible of about 30 cc capacity.

2. Cover the ash with 10 cc of concentrated HCl, allow to digest at the boiling point, covering the crucible with its lid - and continue the digestion until half the liquid has evaporated. Add a further 5 cc of acid and continue boiling to half the bulk. Add again 5 cc of acid till only 2 or 3 cc of liquid remain. Transfer the crucible and lid to a platinum basin or good quality glass dish, 150 cc capacity, containing 75 to 100 cc of hot water. Turn the crucible on its side and digest at the boiling point or just below for about 20 minutes, protecting the liquid from contamination by dust in this and subsequent operations.
3. Remove the crucible and lid, washing clean with hot water and filter through a fine filter paper (Whatman 42) into a platinum basin. Wash the residue five times with hot water, collecting the washings with the filtrate. Evaporate on a water bath.
4. Transfer the wet filter paper and residue to a platinum crucible and after gentle heating incinerate at a dull red heat. Allow to cool and mix the residue thoroughly in the crucible with 4 g of anhydrous Na_2CO_3 . Cover the crucible with its lid and heat by means of an ordinary burner until fusion point is reached. Raise the temperature of fused mass to 1000°C at a rate which avoids excessive turbulence, maintain at this temperature until liquid is

quiescent after which, heat for about 30 minutes at a temperature not below 1100°C .

5. Allow the crucible to cool, then heat rapidly to about 400°C and immediately plunge the lower $\frac{2}{3}$ of the crucible into cold water to loosen the melt. Immerse the crucible in sufficient hot water to cover it, contained in a platinum basin. Add the crucible lid. Cover the basin and slowly add 13 cc of concentrated HCl. Add 1 or 2 drops of H_2O_2 to decompose any manganic acid which may have come from manganates formed during the fusion. Heat the liquid gently to boiling point, and remove the cover glass, washing the underside into the liquid. Lift out the crucible and lid by means of a thin glass rod, washing each into the liquid. Clean the inside of the crucible with water and a rubber tipped glass rod, adding the washings to the liquid. Add 10 cc of a solution of ammonium sulphate.

and

6. Transfer the liquid/precipitate to the vessel in which the acid solution of the ash has been evaporating. Evaporate the whole to dryness in a waterbath.
7. Cool, cover the basin and add 10 cc of concentrated HCl, followed after 2 to 3 minutes by 90 cc of hot water. Remove the cover glass, washing the underside into the liquid. Heat the

liquid to boiling point and maintain it at the boiling point for 10 minutes. Decant the supernatant liquid through a rapid, low ash, filter paper Whatman No. 41, subsequently washing the residue on to the paper. Wash the residue with hot diluted HCl and 3 times with hot water. Evaporate the filtrate to dryness on a water bath. Heat in an oven at 110°C for 1 hour.

(b) Procedure for Both Coal Ash and Gypsum:-

Take 2 gms of gypsum in a beaker. In a second beaker take the solution of coal ash as obtained above and proceed with these samples separately as follows:-

Add 25 cc of 1 + 1 HCl and boil gently on hot plate till the residue is white or remains light coloured on continued boiling. Cool a little and add a few drops of K MnO_4 to oxidise iron completely taking care to add only 1 drop in excess so that the pink colour will fade quickly. Add 200 cc H_2O , 20 cc 1 + 1 H_2SO_4 and 8 gram of ammonium thiocyanate and shake. Titrate with a solution of mercurous nitrate, shaking well throughout the titration, until the red colour of ferric thiocyanate is just discharged.

Standardisation of Mercurous Nitrate:- Take 25 cc of decinormal solution of Ferrous ammonium sulphate, add 20 cc of diluted H_2SO_4 and cool to about 10°C . Add a decinormal solution of K MnO_4 till the iron is oxidised

and there is so small an excess of permanganate that the pink colour fades quickly. Add 8 gm ammonium thiocyanate and allow the solution to attain room temperature.

Titrate with a solution of Mercurous nitrate, shaking vigorously throughout the titration, until the colour of ferric thiocyanate is just discharged.

Calculations:-

(a) Gypsum:-

weight of gypsum taken = 1.988 gm

25 cc of standard Ferric ammonium

sulphate solution = 48.15 cc of mercurous
nitrate solution

1 cc of standard ferric alum.

solution = 0.00796 gm of Fe_2O_3

\therefore 1 cc of Hg No_3 solution = $\frac{25 \times 0.00796}{48.15}$ gm

of Fe_2O_3

= 0.00413 gm Fe_2O_3

Iron contained in gypsum consumes = 0.1 cc of
mercurous nitrate
solution

\therefore % Fe_2O_3 in gypsum:-

= $0.00413 \times 0.1 \times \frac{100}{1.988}$ = 0.02%

(b) Coal Ash:-

weight of watchglass = 15.2917 gm
 weight of watchglass + ash = 15.4950 gm
 weight of ash taken = 0.2033 gm
 No. of cc of HgNO_3 used = 13.1

Standardisation:-

5 cc of standard F.A.S. = 9.9 cc of HgNO_3
 $\therefore 1 \text{ cc of } \text{HgNO}_3 = \frac{5 \times 0.00796}{9.9}$
 $= 0.00402 \text{ gm } \text{Fe}_2\text{O}_3$
 $\therefore \text{Fe}_2\text{O}_3 = 0.00402 \times 13.1 \times \frac{100}{0.2033}$
 $= 25.904\%$

(iv) Determination of SiO_2 , TiO_2 and Al_2O_3 Content of Coal Ash and Gypsum:-

The analysis was done according to standard methods (114) using spectrophotometer No. S.P600 built by Unicam Instrument Co. Nickel crucibles were used in the determinations. Solutions of chemicals liable to corrode glass were kept in polythene bottles to avoid addition of SiO_2 . A microbalance was used for weighing coal ash and gypsum in the spectrophotometric work.

To ensure the stability of the source of illumination in the spectrophotometer a storage battery was used. The amplifier circuit of the instrument was fed by a.c. line. Care was taken to fix the adapter containing the

cells rigidly in the spectrophotometer, as slight shifts in position caused large changes in the fraction of incident light reflected from the test tube surface. The adaptor was adjustable to fix cells of different dimensions.

After switching on the spectrophotometer, some time was given to stabilise the instrument readings. The comparison tube containing the reference blank solution was moved to position. The wavelength selector was adjusted to the desired wave length, e.g. 370 or 600 m.m.u. using blue photocell. Above 637 red photocell can be used. First the dark current switch was moved to adjust the position of the needle to zero and then the "check" knob was moved to bring the position of the needle again to zero with blank solution inserted in position. Then the sample solutions were inserted in position one by one and the readings taken.

Procedure:-

(a) Silica Determinations:-

1. Weigh accurately 0.1 gm of sample, ground to pass a 100 mesh screen. Transfer to a nickel crucible of approximately 75 cc capacity.
2. Add 10 pellets (approximately 1.5 gm) of NaOH.
3. Cover the crucible and heat to dull red for 3 to 5 minutes. Remove from the heat and swirl the melt around the sides of the crucible. Allow to cool.

4. Add approximately 50 cc of distilled water and allow to stand at least 15 to 20 minutes, stirring occasionally with a platinum rod.
5. Transfer the contents of the crucible to a 600 cc beaker containing approximately 400 cc of distilled water and 6 cc of HCl. Scrub the crucible with a rubber policeman and wash any remaining solution or residue into the beaker.
6. Transfer the solution to a 1 litre volumetric flask, make up to volume with distilled water and mix well.

In the determination of SiO_2 , the yellow silico-molybdate complex is reduced to molybdenum blue and the transmission of light is measured at 650 m.m.u. As silica is the predominant constituent in silicate rocks, relatively more precise values are desired for SiO_2 , than for the constituents present in lower concentrations. For this reason sample weighing, volume measurement and spectrophotometer readings were made accurately.

Reagents:-

(a) Ammonium molybdate reagent solution:- Dissolve 75 gm ammonium molybdate in 750 cc of water. Add 100 cc of 1 + 1 H_2SO_4 and make up to one litre in volume. Store in a plastic bottle.

(b) Tartaric Acid solution 10%:- Water solution, stored

in a plastic bottle, 500 ml.

(c) Reducing solution:- Dissolve 7 gm of sodium sulfite in water. Add 1.5 gm of 1-amino-2 naphthol-4 sulfonic acid and stir until dissolved. Dissolve 90 gram of sodium bisulphite in 800 cc of water, and add this solution to the solution above and mix.

Reference Standard Solution:-

A solution is prepared by the method described above, using the National Bureau of Standards sample no. 70 or 99. The nickel crucible should be carefully cleaned with diluted HCl before use to remove any iron, which may have been left on the crucible from the previous fusion. The standard solution should be stored in a plastic bottle and should be prepared fresh if more than a week old.

Procedure:-

1. Pipette 5 cc of prepared sample solution into a 100 cc flask.
2. Add 50 cc water.
3. To another 100 cc volumetric flask, add 50 cc water as a blank.
4. Add 1 cc of the ammonium molybdate reagent to each flask, swirling the flasks during the

additions. Mix well and allow to stand for 10 minutes.

5. Add 4 cc of the tartaric acid solution, swirling the flasks while adding.
6. Add 1 cc of the reductant solution while swirling the flasks, make to volume, mix well and allow to stand at least 30 minutes.
7. Determine the percentage transmission for each solution at 650 m.m.u., using the reagent blank solution as the reference blank solution.

Factor for Calculations: =
$$\frac{\text{Percent SiO}_2 \text{ of comparison standard}}{\text{absorbance of comparison standard}}$$

∴ Percent SiO₂ in sample = Factor x absorbance of sample solution.

(b) Test for TiO₂:-

An extract of gypsum and ash was made by taking 1 gm samples and adding 10 cc 1 + 1 H₂SO₄ and 20 cc of H F in a platinum crucible. After digesting overnight the volume was reduced to 5 cc on a steam bath. Crucible was heated on a burner to the evolution of SO₃ fumes. The crucible was cooled and the contents dissolved in 200 cc volumetric flask. 15 cc of this solution were run into 15 cc of TiO₂ reagent solution (prepared by adding 100 cc

1 + 1 H_2SO_4 , 100 cc H_3PO_4 and 100 cc of 30% H_2O_2 to 700 cc of water and stored in a brown bottle).

No yellow colour developed. Thus titanium was absent from ash and gypsum.

(c) Al_2O_3 Determinations:-

Al_2O_3 is determined by measuring the transmission of light at 370 m.m.u. of the complex of aluminium with ferron (8 hydroxy-7-iodo-5 quinoline sulfonic acid).

Iron and Titanium also form complexes with ferron which affect the absorbance at 370 m.m.u. The effects are proportional to their respective concentrations and are additive so it is possible to apply corrections for them. The correction for TiO_2 is based on the concentration of TiO_2 in the sample as determined. The correction for iron is based on the determination of the effect of iron actually present in the solution, used in the determination of Al_2O_3 . This is necessary because of the partial retention of iron by the nickel crucible used for the NaOH fusion. The effect of iron actually present in the solution can readily be determined because it is the only common ion complexed by ferron which has appreciable absorbance at 600 m.m.u. and the relationship of concentration of iron to absorbance is linear at both 370 m.m.u. and 600 m.m.u.

Reagents:-

Ferron (8-hydroxy-7-iodo-5 quinoline sulfonic acid) solution,

0.2%: water solution, 1000 cc.

Ammonium Acetate Solution, 10%: Water solution, 1000 cc
HCl, 1 + 9 solution.

Standard Fe Solution:- Prepare a solution in which 1 cc contains 0.01 mg of Fe_2O_3 by diluting 10 cc of the standard iron solution $\text{Fe}_2\text{O}_3 = 0.5 \text{ mg/ml}$ to 500 cc with water. The standard iron solution is prepared as follows:-

Weigh 0.699 g of pure iron wire. Dissolve in 50 cc of 1 : 1 HCl. Add 50 cc of H_2SO_4 . Evaporate and heat to fumes of SO_3 , adding approximately 1 cc of HNO_3 as the fuming point is reached. Cool, dilute to 200 ml, and heat until solution is clear. Cool and make up to two litres with distilled water. OR, Pipette 2 cc of standard ferric ammonium sulphate solution (24.11 gm F.A.S/500 cc) into a litre volumetric flask and dilute to the mark with distilled water. This prepared solution contains 0.01592 mg $\text{Fe}_2\text{O}_3/\text{ml}$.

Reference Standard Solution:- The reference standard solution prepared for the determination of SiO_2 is used.

Procedure:-

1. Transfer 10 cc of solution A, 10 cc of the reference standard solution and 10 cc of the standard Fe_2O_3 solution to separate 100 cc

volumetric flasks.

For the first set of samples, and occasionally thereafter, 10 cc of the standard TiO_2 solution is also carried through the procedure.

2. Dilute the solutions in the flasks to approximately 70 cc. Add approximately 70 cc of distilled water to another 100 cc volumetric flask to be used for the preparation of a reagent blank solution.
3. Add 1 cc of HCl (1 + 9) to each flask and mix.
4. Add 10 cc of the ammonium acetate solution to each flask while swirling the flask.
5. Finally add 10 cc of the ferron solution while swirling the flask. Make up to volume, mix well, and allow the solutions to stand at least one hour.
6. Transfer 50 cc of each solution to comparison cells and determine absorbance at 370 m.m.u., using the reagent blank solution as the reference blank.
7. Determine absorbance at 600 m.m.u. for each solution, except the reference standard solution and the solution containing the standard TiO_2 , using the reagent blank solution as the reference blank.

Method of Calculations:-

1. Factor for iron correction

$$= \frac{\text{absorbance of standard Fe}_2\text{O}_3 \text{ at } 370 \text{ m}\mu}{\text{absorbance of standard Fe}_2\text{O}_3 \text{ at } 600 \text{ m}\mu}$$

2. Calculate the corrections for iron effect.

$$\begin{aligned} \text{The iron correction} &= \text{Fe}_2\text{O}_3 \text{ correction factor} \times \\ &\quad \text{absorbance of sample solution} \\ &\quad \text{at } 600 \text{ m}\mu \\ &= \text{absorbance at } 370 \text{ m}\mu \text{ due} \\ &\quad \text{to iron} \end{aligned}$$

3. Subtract the Fe_2O_3 correction from the absorbance values obtained for the sample solution at 370 m μ .

4. Calculate the factor for Al_2O_3 :

$$\text{Factor} = \frac{\text{concentration of Al}_2\text{O}_3 \text{ in reference standard}}{\text{absorbance at } 370 \text{ m.}\mu.}$$

5. Calculate percent Al_2O_3 .

$$\% \text{ Al}_2\text{O}_3 = \text{factor} \times \text{corrected absorbance, step 4.}$$

NOTE: Soda Feldspar sample no. 99 supplied by U. S. Bureau of Standards, Department of Commerce, contains 68.66% SiO_2 and 19.06% Al_2O_3 .

Absorbance of gypsum at
600 m.m.u. = 0.000

Absorbance of ash at
370 m.m.u. = 0.515

Absorbance of ash at
600 m.m.u. = 0.117

Absorbance of Fe solution
at 600 m.m.u. = 0.112

Absorbance of Fe solution
at 370 m.m.u. = 0.145

Standard iron solution contains = 0.01592 mg Fe_2O_3 per cc

Correction factor for Fe = $\frac{0.145}{0.112}$ = 1.294

(a) Coal Ash:-

Absorbance due to Fe at 370 m.m.u. = 0.117 x 1.294
= 0.1515

∴ absorbance due to Al_2O_3 at 370 m.m.u = 0.515 - 0.1515
= 0.3635

∴ Al_2O_3 in Ash = $\frac{19.06 \times 0.3635 \times 0.049873}{0.237 \times 0.04967}$

= 29.35%

(b) Gypsum:-

$$\begin{aligned} \text{Al}_2\text{O}_3 \text{ in gypsum} &= 19.06 \times \frac{0.003}{0.237} \times \frac{0.049873}{0.05417} \\ &= 0.222 \% \end{aligned}$$

(v) Results:-

Gypsum:-

Free water	=	0.0746 %
Combined water	=	20.874 %
Silica	=	0.00 %
Fe ₂ O ₃	=	0.02 %
Al ₂ O ₃	=	0.222 %
Titania	=	0.00 %
CaSO ₄ .2H ₂ O	=	99.758 %

Ash:-

Silica	=	43.084%
Fe ₂ O ₃	=	25.904 %
Al ₂ O ₃	=	29.35 %
Titania	=	0.00 %
SO ₃	=	1.011 %
CaSO ₄	=	1.718 %

CHAPTER VII.

Standardisation of Analytical Methods and Procedure For The Run:

I. Standardisation of Analytical Methods:-

A. Proposed Method:-

Calcium sulphate when heated with carbon, silica and metallic oxides at high temperatures, gives rise to the evolution of oxides of sulphur, in oxidising atmospheres. When the time of heating is small some sulphide is also formed. In non-oxidising atmospheres also, the problem of the estimation of sulphur dioxide and calcium sulphide was to be solved.

It was decided to absorb the oxides of sulphur in $10 \text{ NH}_2\text{O}_2$, to convert them into sulphuric acid and estimate them volumetrically.

The pellet was taken out of the reactor and the calcium sulphide contained in it was estimated by evolving the H_2S with acid and absorbing it in a suitable solution and then estimating it volumetrically.

B. Problems Associated with the Determination of Oxides of Sulphur Absorbed in Hydrogen Peroxide:-

Hydrogen peroxide is usually stabilised with an acid. While determining the acid content of H_2O_2 supplied

by Laporte Chemicals Pty., it was found to be stabilised by benzoic acid. Carbon dioxide produced from carbon in the pellet, is also absorbed in H_2O_2 giving rise to carbonic acid. The presence of these weak acids in a powerful oxidising agent like H_2O_2 introduced the problem of accurately estimating the sulphuric acid produced from the oxides of sulfur, evolved from the pellet. A suitable indicator was required to estimate the acidity produced by absorbing the gases in (a) H_2O_2 containing a known excess of standard NaOH solution (b) or neutral H_2O_2 .

The following indicators were found unsuitable:

- (a) Bromothymol blue.
- (b) Methyl red.
- (c) Methyl orange.
- (d) Methyl orange + Indigo-Carmine.
- (e) Methyl yellow.
- (f) Dimethyl yellow.
- (g) Methyl yellow + methylene blue.
- (h) Neutral red + methylene blue.
- (i) Bromo cresol purple.
- (j) Rosolic acid (Strongly attacked by H_2O_2).

The two indicators which proved good in acidic H_2O_2 are these:-

(a) Methyl red + Methylene blue.

(b) Methyl red + Bromo cresol green.

Trials were made to see how they responded in alkaline H_2O_2 , as there was no reference to it in the literature. They appeared to work alright in H_2O_2 made alkaline with standard NaOH solution to which 1 cc of N/10 Sodium-carbonate solution was added, on titrating against standard N/10 HCl, but under actual experimental conditions they did not respond. Instead of one drop, 5 cc of N/10 HCl were required for a colour change. To eliminate the possibility of interference due to benzoic acid, hydrogen peroxide was prepared from sodium peroxide. About 7 grams of Na_2O_2 were dissolved in 100 cc distilled water to give 10 NH_2O_2 solution, the alkalinity of which ^{is} approximately equal to 2N NaOH solution, and sulphur dioxide was absorbed in it. The titration made against standard HCl using above indicators did not give a sharp end point. Even when the normalities of two solutions were the same the titration curve was flat.

Thus sulphur dioxide was absorbed in neutral hydrogen peroxide and sulphuric acid was titrated against standard NaOH solution using Methyl red + bromocresol green as indicator. It is prepared by mixing three parts of 0.1% Bromocresol green solution in alcohol and

one part of 0.2% methyl red solution in alcohol. The colour change is exceptionally sharp at pH 5.1. The colour in acidic medium is wine red and in alkaline medium green. The indicator is stable towards H_2O_2 .

Methyl red screened with methylene blue has a red violet colour at pH 5.2, dirty blue at 5.4, dirty green at 5.6, and thus not as sharp in colour change as when screened with bromo-cresol green.

C. Determination of the Sulphide Content:--

From the pellets heated in the furnace, the amount of sulphide sulphur can be estimated by evolving the sulphur as H_2S , which can be estimated by absorbing in the solution of a suitable substance and back titration.

To find a suitable volumetric method applicable in determining small amounts of evolved H_2S , the following methods were tried.

(a) H_2S was absorbed in a known excess of standard iodine solution and titrated against sodium thiosulphate solution using sodium starch glycollate as indicator. The method was defective as the precipitated sulphur enclosed a portion of iodine which escaped titration.

(b) Evolved H_2S was absorbed in a standard sodium arsenite solution prepared by dissolving arsenious oxide in 10% NaOH solution, acidified with HCl, filtered,

neutralised with sodium bicarbonate, and titrated the excess of arsenious acid against iodine, using sodium starch glycollate as indicator.

In this method, the filtration of arsenious sulphide becomes necessary in each titration, making it cumbersome, moreover the indicator takes a few drops to show the colour change.

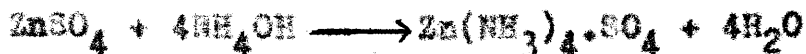
(c) KIO_3 was used as an oxidising agent in method (b) keeping the acidity of the solution between 3N and 5N, as with too high acidity the reaction took place very slowly. No suitable reversible indicator was available, while it was difficult to get concordant results using chloroform or carbon tetrachloride in detecting the end point by the loss of purple colour in their layers.

(d) Potassium bromate seemed very promising as oxidising agent in presence of high acidity, using α -naphthoflavone or p-ethoxychrysoidine as internal indicators. In this also it was found that the filtration of arsenious sulphide was necessary, as due to the strong oxidising nature, it oxidised the sulphide as well as the arsenious acid.

(e) To avoid the filtration of the colloidal precipitate the following were tried to absorb H_2S :-

- (1) Ammoniacal-cadmium chloride solution:- It was soon found that this solution was affected by light and hence unsuitable.

- (11) Ammonical zinc sulphate:- This solution proved useful and was very effective.



Modified Method:-

The H_2S evolved was absorbed in ammoniacal zinc sulphate solution, then acidified with excess of HCl , KBr solution added, and titrated against Potassium bromate using α -naphthoflavone as indicator, which was more sensitive than even p -ethoxychrysoidine. α -naphthoflavone indicator was prepared by dissolving 0.1 gm in 100 cc of ethyl alcohol.

Thus in this method, the use of iodine and iodides, iodate and iodide, starch and irreversible indicators was entirely avoided. It was found that iodate and iodide mixture evolved iodine even without acidification.

II. Procedure For The Run:-

A. Pellet Making:-

The dry constituents powdered to -200 mesh were accurately weighed, and thoroughly mixed with a pestle and mortar. The mixture so obtained was dry-pressed in the pellet making machine and the pellets dried overnight at 45°C to eliminate any moisture. The pellets were then weighed in the platinum boats and kept ready for feeding

in the reactor.

The use of water in any form, while making the pellets was avoided. One pellet was struck each time. To make a good pellet it was kept pressed in the machine for a minute. They were handled throughout by a spatula.

B. Production and Regulation of Atmospheres in the Reactors:-

For oxidising atmospheres, air and oxygen were admitted in the reactor in the ratio 10 : 1 at a rate of 100 cc/minute. Air was first passed through the scrubber to remove CO_2 and dust particles and then through U-tubes containing silica gel and phosphorous pentoxide to remove the traces of water. Its flow was measured by a calibrated flowmeter and then mixed with purified oxygen in a T-tube wherefrom it passed through a rubber tube, into the reactor. The oxygen was purified by passing through a bubbler containing conc. sulphuric acid, and a U-tube containing ascarite. Its flow was measured in a second flowmeter and then mixed with air in the T-tube.

For neutral atmospheres oxygen free nitrogen was employed at a rate of 100 cc per minute.

C. Temperature Adjustment:-

The temperature was then very carefully adjusted and care was taken to avoid fluctuations during the run.

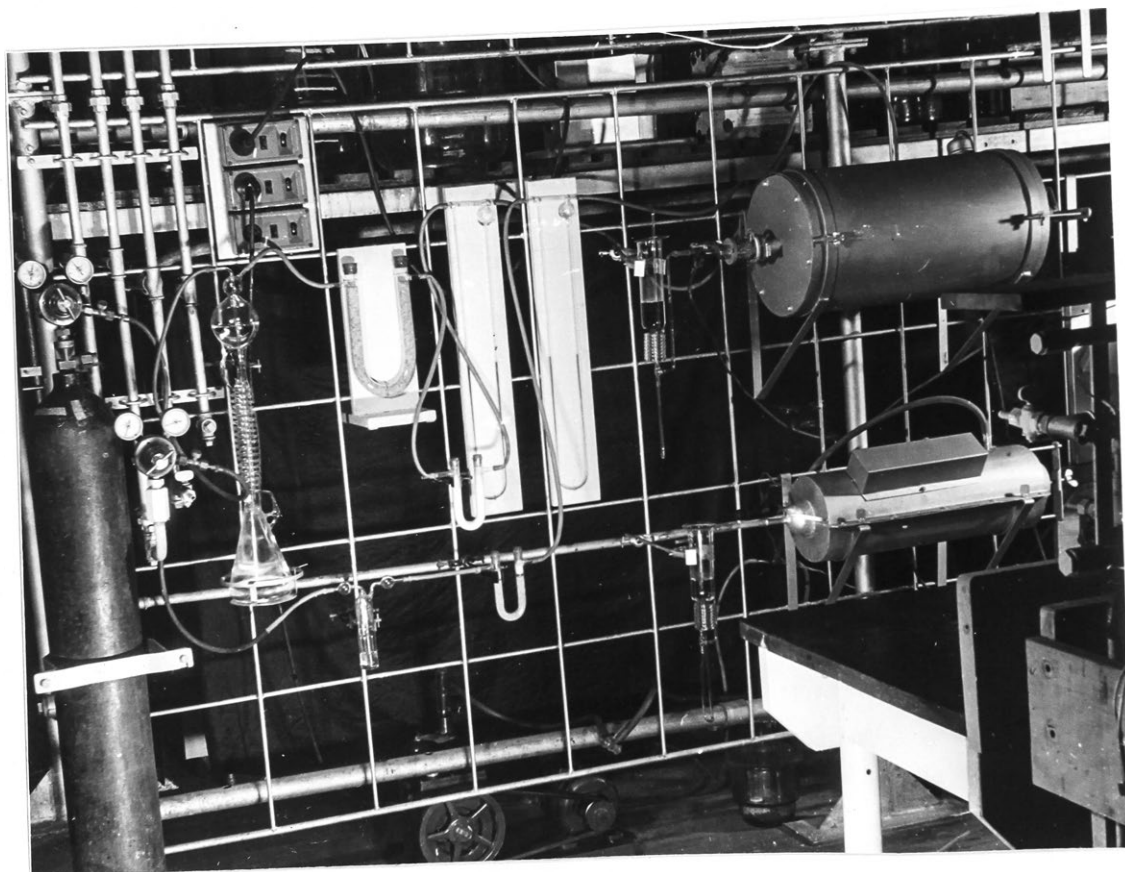


Fig. 7.2.1

Arrangement of the equipment for the
study of decomposition of gypsum in
oxidising atmosphere.

The practice of giving sufficient time to reach the balance before the start of a series of runs at a particular temperature was found profitable. The temperature was raised and lowered slowly to avoid cracking of the mullite tube and was kept at 730°C , when the reactor was not used.

D. Insertion of Boat Containing the Pellet in the Reactor and Absorption of the Evolved Gases:-

The reactor was flushed with the gases to produce the desired atmospheres and the absorber containing 100 cc of neutralised $10\text{ NH}_2\text{O}_2$, was connected to the outlet tube. The gas flow and the temperature were re-checked. The inlet endplate was removed quickly and the boat containing the pellet was pushed inside the reactor by means of a silica launching rod carrying a molybdenum wire bent at right angles to form a hook and tied to one end of the rod by means of a thin molybdenum wire. The measurements of the launching device were as follows:-

Length of rod -	20 inches
Thickness of rod -	$1/4$ "
Length of hook protruding from the rod -	1 "
Length of the short arm of the hook -	$5/16$ "
Thickness of wire forming the hook -	18 S.W.G.

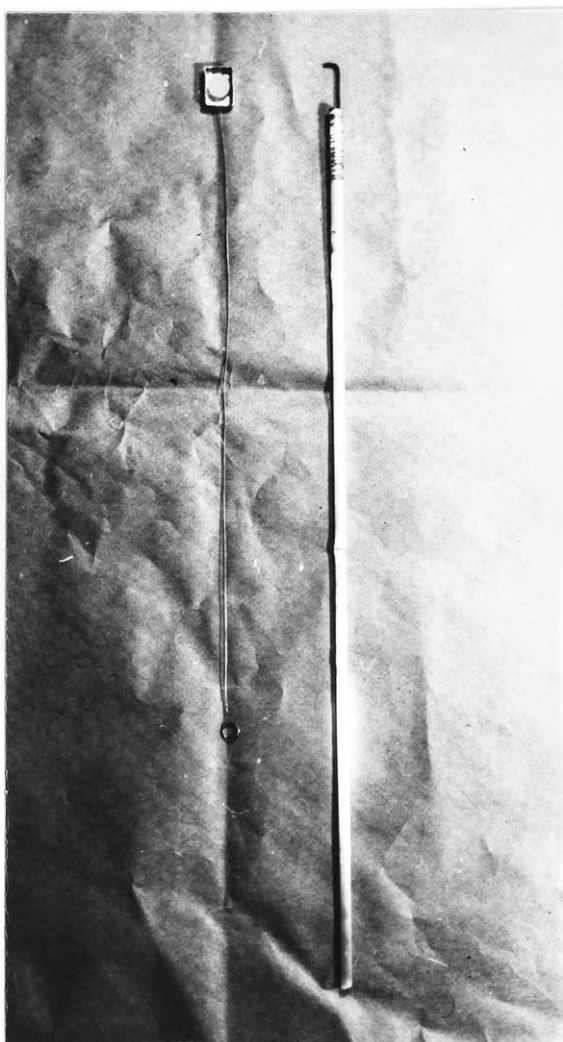


Fig. 7.2.2
Platinum boat and the launching
device.

Simultaneously with the pushing of the boat to the middle of the hot portion of the reactor where it rested against the end of the thermocouple sheath, the knob of the stop watch was pressed to keep exact time. As soon as the time was over the boat was withdrawn from the reactor quickly, and the endplate of the reactor screwed on again. Withdrawal of the boat was done by means of a 16 s.w.g. platinum wire tied to the boat through a hole drilled in its side, with the free end of the wire rolled into a knob to facilitate handling. The author believes that the withdrawal from the hot zone was as quickly done as dropping of a pellet from a vertical reactor. The length of the tube was large enough to prevent the escape of evolved gases during the insertion and withdrawal of the boat, which was borne out by concordant results. Withdrawal of the boat and clamping of the end plate took 5 seconds. The reactor tube was then flushed for 20 minutes to drive off the gases into the absorber and the sulphuric acid produced titrated against standard alkali solution.

D. Fog Formation:-

At higher temperatures, e.g. 1400°C , fog was produced in the absorber. It gave negative tests for SO_3 and was found to be H_2O_2 mist carrying a bit of acidity with it. Three absorbers were used in series to make sure that no fog escaped.

F. Removal of CO_2 :-

CO_2 contained in air was scrubbed off before entering the reactor. Some CO_2 obtained from the carbon contained in the pellet, was absorbed in H_2O_2 making it acidic, but it was completely removed by the bubbling of carrier gases during the flushing period of twenty minutes.

G. Procedure for the Titration of Sulphuric Acid Formed in the Absorber:-

It was first of all made sure that the sulphur absorber was perfectly clean and otherwise in good condition. 100cc of $10\text{NH}_2\text{O}_2$ were transferred to the absorber. Six drops of the Bromocresol green - methyl red indicator were added. The solution was stirred by connecting the absorber to the reactor and employing the CO_2 free gas stream coming out of it for stirring. Wine red colour developed due to the benzoic acid present in the H_2O_2 and 0.01 N CO_2 free solution was used dropwise to neutralise the acidity, shown by the just dispelling of the wine red colour. This was taken as the end point. If this point was overtitrated, one or more drops of 0.01 N CO_2 free HCl standardised ^{were} added and adjusted the end point with NaOH solution.

Next, checked the rates of flow of the sweeping gas mixture (100 cc/minute) and adjusted the temperature. The boat containing the pellet was then admitted in

the hottest zone of the reactor along with the wire tied to the boat and the evolved gases were absorbed and converted to H_2SO_4 by H_2O_2 solution in the absorber. After the required interval of time the boat was pulled out quickly by means of the attached wire, on to a ceramic receiving tray, held just under in front of the opening. The reactor was sealed again by screwing on the end plate and any remaining evolved gases swept for 20 minutes. Sulphuric acid formed in the absorber turns the colour of the indicator wine red.

After 20 minutes, the standard NaOH solution was added to the absorber until the wine red colour just disappeared. Rinsed three times through the inlet arm of the absorber by means of a stream of CO_2 free water from a wash bottle, and the bubbling continued each time accompanied with neutralisation. The titrated solution was poured from the absorber and replaced with another 100 cc of 10 NH_2O_2 solution preparatory to another determination. No rinsing of absorber was necessary.

H. Procedure for the Determination of the Sulphide Content:-

Preparation of the absorption solution of Ammoniacal zinc sulphate:-

200 gms of zinc sulphate were dissolved in 1000 cc of H_2O and 1000 cc of strong NH_4OH were added,

and filtration done after 24 hours.

Procedure:-

The H_2S generator was swept free of air by a stream of oxygen free nitrogen obtained from a cylinder. The boat containing the pellet was dropped in it and 30 cc of 6N HCl were quickly dropped through the thistle funnel and the absorber containing 10 cc of ammoniacal zinc sulphate solution and 40 cc of water immediately attached to the generator. Oxygen free nitrogen was then passed at a slow rate (ca. 100 cc/minute) through the equipment and the generator was heated on a very low flame for ten minutes. Distillation of HCl with H_2S was avoided as much as possible. H_2S turned ammoniacal zinc sulphate solution milky. Any trace of H_2S left in the generator was then swept away by the N_2 to the absorber after which the nitrogen flow was stopped and the absorber disconnected. The solution in the absorber was cooled under a tap and then poured in a beaker. The inlet tube and the frit glass along with the absorber were rinsed three times and the rinsings added to the beaker. The contents of the beaker were diluted with distilled water to 200 cc, and 40 cc of 6NHCl were added to liberate H_2S , followed by 10 cc of 10% KBr solution, 1 cc of α -naphthoflavone indicator and titration was done against standard potassium bromate solution, until the colour of the solution changed to orange. The colour change was sharp.

Fe_2O_3 , when present in the pellet, formed FeCl_3

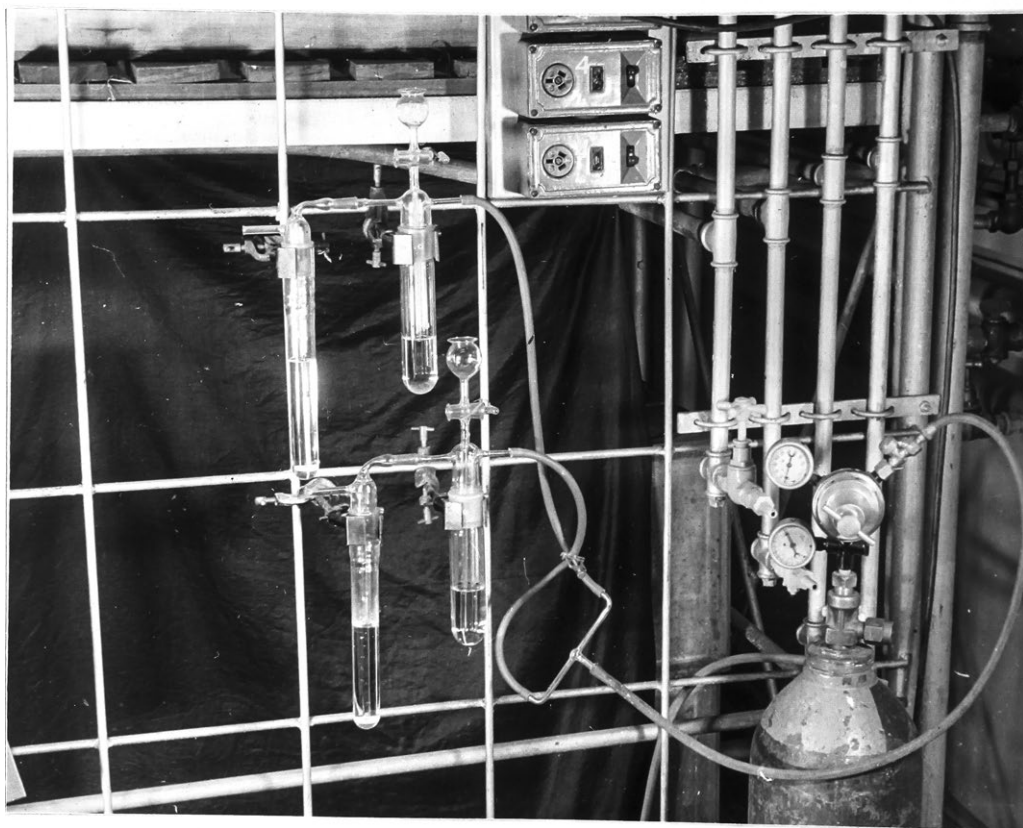


Fig. 7.2.3
Equipment for the estimation of
sulphide sulphur.

with the hydrochloric acid, which oxidised H_2S to S and attacked the platinum boats according to the following equation (63):-



Therefore, whenever coke or Fe_2O_3 was used as a constituent of the pellet, H_2S was evolved with the help of 20 cc of concentrated HCl to which 3 cc of 10% stannous chloride solution was added to reduce the ferric iron into ferrous state. In practice stannous chloride solution was added first, followed by conc. HCl . Tin sulphide formed decomposed in the presence of hot, concentrated HCl to give H_2S which was carried over by the nitrogen stream to the absorber.

Whenever the amount of sulphide in the pellet was appreciable 20 cc of zinc ammonian sulphate solution were employed in the absorber, and after absorption 50 cc of 6N HCl were added to liberate the H_2S . Theoretically the minimum amount of water in which H_2S produced from 1 gm of CaS will remain soluble is 124.2 gm.

In order to avoid clogging of the pores of the frit glass, it was kept dipped in 6N HCl and washed with distilled water before use.

I. Problem of melts obtained at High Temperatures:-

Whenever melts were obtained in the boats after heating pellets of particular compositions, it was found that they stuck to the boat and were difficult to scratch off, the hardness being 6 - 7 Mohs. The dentist's scaler No. 149 made of stainless steel was unable to remove them. Prolonged boiling with HCl made them a bit brittle, after which the boats were heated on the Bunsen flame and then quenched in water. The scaler could then chip off the melts and the boats were cleaned free of them.

J. Method of Calculations:-

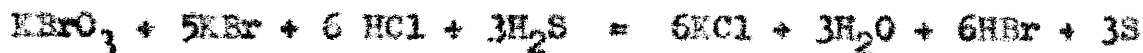
(1) For evolved sulphur:-

$$\begin{aligned}
 (i) \quad 1 \text{ cc of } 0.1N \text{ NaOH solution} &= 1 \text{ cc of } 0.1 N \\
 &\quad \text{H}_2\text{SO}_4 \text{ solution} \\
 &= 0.0049016 \text{ gms of} \\
 &\quad \text{H}_2\text{SO}_4 \\
 &= 0.0049016 \times \frac{32}{98.016} \text{ gm} \\
 &\quad \text{of sulphur} \\
 &= 0.00160026 \text{ gm of sulphur.}
 \end{aligned}$$

$$\begin{aligned}
 (ii) \quad 1 \text{ cc of } 0.1N \text{ NaOH solution} &= 0.00160026 \times \frac{136.146}{32} \\
 &= 0.0068084 \text{ gm} \\
 &\quad \text{desulphurised CaSO}_4
 \end{aligned}$$

(iii) 1 cc of 0.01 N NaOH solution = 0.00068084 gm
desulphurised CaSO_4

(2) For sulphide sulphur:-



167.012

102.048

$$\begin{aligned} (1) \quad 1 \text{ cc of } 0.1\text{N}\text{KBrO}_3 &= \frac{102.048}{167.012} \times 0.002784 \\ &= 0.001701 \text{ gm of } \text{H}_2\text{S} \\ &= 0.00160018 \text{ gm of sulphide S} \\ &= 0.00160018 \times \frac{72.146}{32} \text{ gm of CaS} \\ &= 0.003607705 \text{ gm of CaS} \end{aligned}$$

(ii) 1 cc of 0.01N KBrO_3 = 0.0003607705 gm of CaS.

Desulphurisation has been calculated on the amount of CaSO_4 present in the synthetic or mineral gypsum.

Use of factors has also been made in calculating the amount of CaSO_4 in the pellet as well as the calcium

sulphate equivalent to the weight of sulphur in the coke contained in the pellet, when coke was one of the constituents. Wherever CaS was present, the desulphurisation was calculated, on the basis of the combined S present in CaSO_4 and CaS at the start. The factors were calculated on one gram pellet - weight basis, which can be multiplied by the actual weight of the pellet and the exact value obtained. The calculations of these factors have been shown at appropriate places in the next chapter.

CHAPTER VIII.

STUDY OF SOLID-SOLID REACTIONS, CLINKER AND MECHANISM OF REACTIONS.

I. Study of solid-solid reactions:-

Theoretical Considerations:-

In oxidising atmospheres, the final products of reaction, of carbon and silica, with calcium sulphate are given by the following equations:-



Thus at suitable temperatures 3 moles of CaSO_4 will be decomposed completely with one mole of C and one mole of SiO_2 giving sulphur dioxide; and two moles of lime will combine with one mole of mono-calcium silicate giving tricalcium silicate, which is the principal constituent of clinker. The above ratios of the reactants should give the maximum amount of SO_2 in the evolved gases and the maximum amount of tri-calcium silicate in the clinker.

Studies were thus directed to start with a

system containing the constituents in the above theoretical ratios and making appropriate changes in the subsequent systems, in the light of the information obtained from the preceding ones. As during the early course of the reaction, carbon reduced CaSO_4 to the sulphide state, the estimation of CaS formed in the pellet after heating, was done for each run. This determination was necessary because CaS should not exist in a good clinker, moreover the excess of it causes fusion in the kiln.

During the course of the studies both synthetic and mineral gypsums were used. The first one has been denoted by the formula and the second one by the word gypsum.

Early trials:-

Early trials for finding out the best time intervals for following the rates of reactions at 1400°C gave the following intervals; 1 minute, 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 2 hours and 3 hours.

In most cases the interesting portions of the curves were obtained up to 20 minute intervals, but wherever found necessary the reactions were carried to completion. After 20 minutes the curves became almost a straight line.

The temperature for drying the pellets should not exceed 45°C . Five systems had to be repeated

because the pellets on being dried at 80°C had lost some water of crystallisation.

In the systems to follow, the ratios represent the composition of the reaction mixtures. A known amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was first weighed and the amounts of other constituents to be added, were calculated in the given ratios, on the basis of this weight. Only in cases where B.P.C. CaS (already containing 37.411% CaSO_4), was used as a constituent, the weight of CaS was used as a basis to adjust the weight of gypsum to be added. After weighing the rest of the constituents, the mixture was made with the help of a glass pestle and mortar; the pellets were then struck, dried overnight, weighed in a numbered platinum boat and heated in the reactor for the given time intervals, to obtain the rates of reactions.

All systems in Section I were studied in oxidising atmospheres.

System I.



Weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ taken = 34.1453 gm.

Amount of silica required in the mixture = $60.06 \times \frac{34.1453}{516.534}$ gm

= 3.9700 gm.

Amount of C required in the mixture = $12.01 \times \frac{34.1453}{516.534}$ gm

= 0.7939 gm

$$\begin{aligned}\text{Weight of CaSO}_4 \text{ in 1 gm. tablet} &= \frac{408.438}{588.604} \times 1 \\ &= 0.6939 \text{ gm.}\end{aligned}$$

At 600°C, the pellets of System I were heated for 5, 10, 15, 20, 25 and 30 minutes time intervals. The decomposition was not apparent, excepting the burning of the carbon content.

Table 8.1.1.

System I.

 $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ C}$

800°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc N/100 NaOH used	Sulphide tit- ration cc N/100 KBrO_3 used
Wt. of boat = 5.8820 do. + pellet= 6.6442	5	0.8	nil
Wt. of boat = 6.0468 do. + pellet= 6.8870	10	0.9	nil
Wt. of boat = 6.0502 do. + pellet= 6.7958	15	0.8	nil
Wt. of boat = 5.8100 do. + pellet= 6.4836	20	0.75	nil
Wt. of boat = 6.2212 do. + pellet= 6.8277	25	0.65	nil
Wt. of boat = 5.8920 do. + pellet= 6.5074	30	0.65	nil

Table 8.1.2

System I



Weight of CaSO_4 in 1 gm pellet = 0.6939 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Desulfurised CaSO_4 (gm)	% Desulfurised CaSO_4	CaS formed (gm)	% CaS formed
5	0.7622	0.5289	0.0005447	0.1030	nil	nil
10	0.8402	0.5830	0.0006128	0.1051	nil	nil
15	0.7456	0.5174	0.0005447	0.1053	nil	nil
20	0.6736	0.4674	0.0005106	0.1092	nil	nil
25	0.6065	0.4209	0.0004425	0.1051	nil	nil
30	0.6154	0.4270	0.0004425	0.1063	nil	nil

Table 8.1.3.

System I

 $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ C.}$

1000°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc N/100 NaOH used	Sulphide tit- ration cc N/100 KBrO_3 used
Wt. of boat = 6.0719 do. + pellet= 6.6891	5	12.15	0.5
Wt. of boat = 6.2208 do. + pellet= 6.8773	10	13.5	nil
Wt. of boat = 5.9154 do. + pellet= 6.5600	15	12.7	0.1
Wt. of boat = 6.0586 do. + pellet= 6.8019	20	19.6	nil
Wt. of boat = 5.8816 do. + pellet= 6.4758	25	15.75	nil
Wt. of boat = 6.0463 do. + pellet= 6.7852	30	20.6	nil

Table 8.1.4.

System I.

$$3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ C.}$$

$$\text{Weight of CaSO}_4 \text{ in 1 gm pellet} = 0.6939 \text{ gm}$$

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Desulfurized CaSO_4 (gm)	% Desulfurized CaSO_4	CaS formed (gm)	% CaS formed
5	0.5172	0.4283	0.008272	1.931	0.0001804	0.042
10	0.6565	0.4555	0.009191	2.018	nil	nil
15	0.6446	0.4473	0.008647	1.933	0.00003608	0.008
20	0.7433	0.5158	0.01334	2.586	nil	nil
25	0.5942	0.4123	0.01072	2.600	nil	nil
30	0.7389	0.5127	0.01403	2.736	nil	nil

Table 8.1.5.

System I.

 $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ C.}$

1200°C.

Weights (gm)	Time (mts)	H_2SO_4 tit-	Sulphide tit-
		ration cc N/10 NaOH used	ration cc N/100 KBrO_3 used
Wt. of boat = 6.0721	1	6.3	60.5
do. + pellet= 6.7264			
Wt. of boat = 6.2211	3	11.15	2.5
do. + pellet= 6.7828			
Wt. of boat = 5.9157	5	14.85	1.0
do. + pellet= 6.5350			
Wt. of boat = 6.0591	10	15.55	nil
do. + pellet= 6.7016			
Wt. of boat = 5.8819	15	18.3	nil
do. + pellet= 6.6204			
Wt. of boat = 6.0466	20	15.55	nil
do. + pellet= 6.6645			
Wt. of boat = 6.0088	25	14.2	nil
do. + pellet= 6.5710			
Wt. of boat = 6.0501	30	15.6	nil
do. + pellet= 6.6656			

Table 8.1.6.

System I.

 $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ C.}$ Weight of CaSO_4 in $\frac{1}{2}$ gm pellet at 1200°C = 0.6939 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Desulfurised CaSO_4 (gm)	% Desulfurised CaSO_4	CaS formed (gm)	% CaS formed
1	0.6543	0.4540	0.04289	9.447	0.02183	4.808
3	0.5617	0.3898	0.07591	19.474	0.0009019	0.231
5	0.6193	0.4297	0.1011	23.526	0.0003608	0.084
10	0.6425	0.4456	0.1059	23.755	nil	nil
15	0.7385	0.5124	0.1246	24.317	nil	nil
20	0.6179	0.4288	0.1059	24.697	nil	nil
25	0.5622	0.3901	0.09668	24.783	nil	nil
30	0.6155	0.4271	0.1062	24.865	nil	nil

SYSTEM 1.
3 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: 1 Silica : 1 C

1200°C.

(Oxidising Atmosphere)

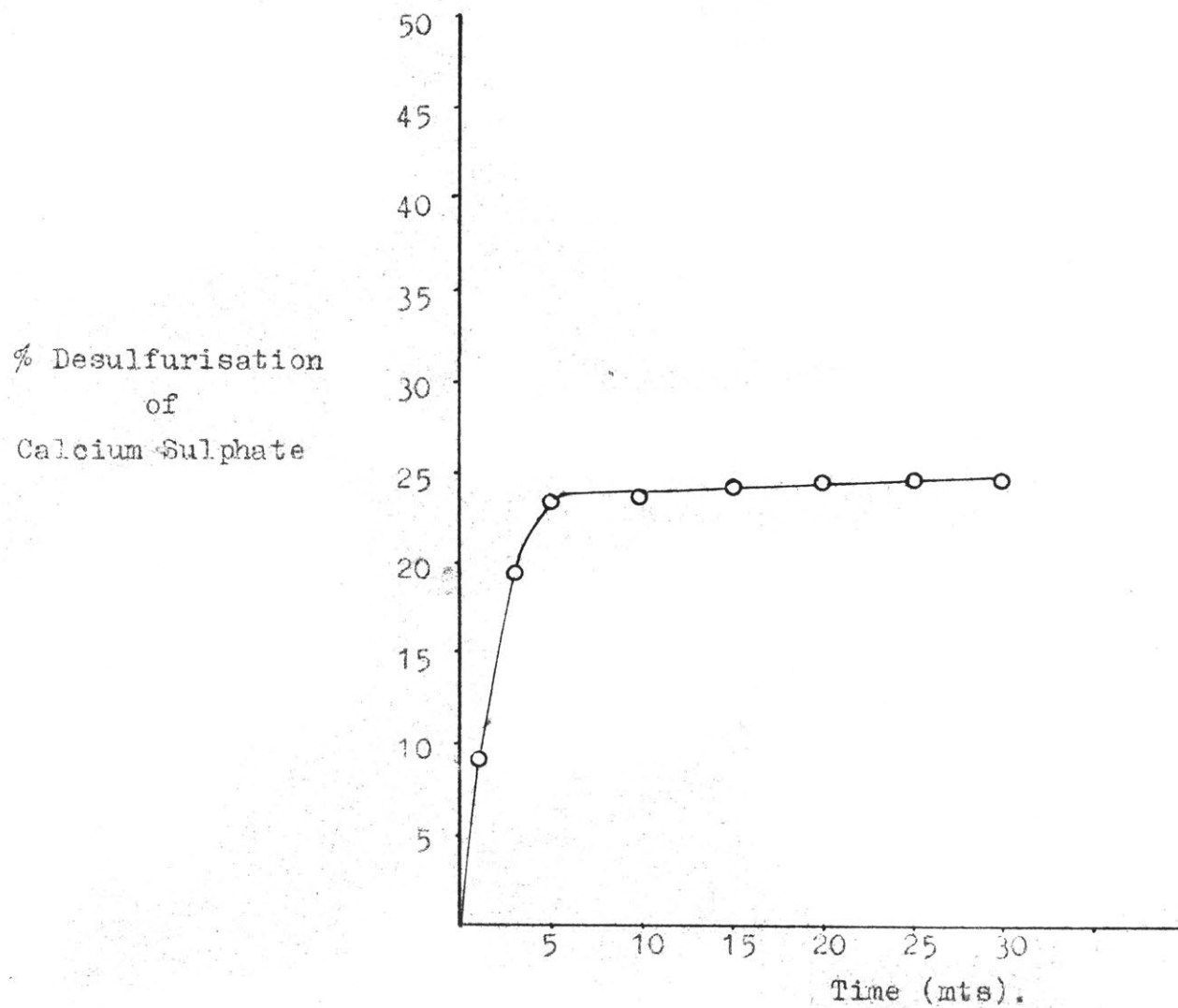


Fig. 8.1.1

Table 8.1.7.

System I.

 $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ C.}$

1400°C.

Weights (gm)	Time	H_2SO_4 tit- ration cc 0.1N NaOH used	Sulphide tit- ration cc 0.01 N KBrO_3 used
Wt. of boat = 6.0536	1	25.7	1.2
do. + pellet= 6.8090	mt.		
Wt. of boat = 6.2084	1	25.7	1.4
do. + pellet= 6.9825	mt.		
Wt. of boat = 5.8962	5	35.7	nil
do. + pellet= 6.6697	mts.		
Wt. of boat = 6.0336	5	35.1	nil
do. + pellet= 6.7662	mts.		
Wt. of boat = 5.8584	5	35.7	nil
do. + pellet= 6.5931	mts.		
Wt. of boat = 6.1019	10	40.75	nil
do. + pellet= 6.8924	mts.		
Wt. of boat = 5.9883	10	39.75	nil
do. + pellet= 6.7684	mts.		
Wt. of boat = 6.0171	20	44.6	nil
do. + pellet= 6.8025	mts.		
Wt. of boat = 5.7910	20	44.4	nil
do. + pellet= 6.5708	mts.		

Table 8.1.7 (cont'd)

Weights (gm)	Time	H ₂ SO ₄ tit- ration cc 0.1N NaOH used	Sulphide tit- ration cc 0.01N KBrO ₃ used
Wt. of boat = 5.8775	30	45.4	nil
do. + pellet= 6.6058	mts.		
Wt. of boat = 6.0521	30	47.1	nil
do. + pellet= 6.8174	mts.		
Wt. of boat = 6.0555	1hr.	53.2	nil
do. + pellet= 6.7705			
Wt. of boat = 6.2056	1hr.	57.45	nil
do. + pellet= 6.9907			
Wt. of boat = 5.8915	2hrs.	63.9	nil
do. + pellet= 6.6642			
Wt. of boat = 6.0989	2hrs.	71.0	nil
do. + pellet= 6.9543			
Wt. of boat = 5.8568	3hrs.	74.6	nil
do. + pellet= 6.6693			
Wt. of boat = 5.9783	3 hrs	85.9	nil
do. + pellet= 6.6966			

Observations:-

Up to 1200°C, no melting took place, but at 1400°C. the pellets melted in the boats, after heating for 5 minutes and over. The molten mass, spread along the sides of the boats, making it hard to clean them.

It was concluded that the melting occurred due to the early burning of carbon, and hence in System II two moles of carbon were added instead of one.

Table 8.1.8.

System I.



Weight of CaSO_4 in 1 gm pellet = 0.6939 gm.

Time	Weight of Pellet (gm)	Weight of CaSO_4 in Pellet (gm)	Weight of Desulfurised CaSO_4 (gm)	% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
1 mt.	0.7554	0.5242	0.1750	33.384	0.0004329	0.083
1 "	0.7741	0.5371	0.1750	32.582	0.0005051	0.094
5 "	0.7735	0.5367	0.2499	46.562	nil	nil
5 "	0.7326	0.5084	0.2390	47.010	nil	nil
5 "	0.7347	0.5098	0.2431	47.685	nil	nil
10 "	0.7905	0.5485	0.2774	50.574	nil	nil
10 "	0.7801	0.5413	0.2706	49.991	nil	nil
20 "	0.7854	0.5450	0.3037	55.785	nil	nil
20 "	0.7798	0.5411	0.3023	55.868	nil	nil
30 "	0.7283	0.5054	0.3091	61.159	nil	nil
30 "	0.7653	0.5310	0.3207	60.395	nil	nil
1 hr.	0.7200	0.4996	0.3622	72.498	nil	nil
1 "	0.7851	0.5448	0.3911	71.788	nil	nil

Table 8.1.8 (cont'd)
System I.

Time	Weight of Pellet (gm)	Weight of CaSO_4 in Pellet (gm)	Weight of Desulfurised CaSO_4 (gm)	% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
2 hrs.	0.7727	0.5362	0.4351	81.145	nil	nil
2 "	0.8554	0.5936	0.4834	81.435	nil	nil
3 "	0.8125	0.5638	0.5079	90.085	nil	nil
3 "	0.7183	0.4984	0.4487	90.028	nil	nil

System II.



Weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ taken = 30.2677 gm.

Amount of SiO_2 required in the mixture = $60.06 \times \frac{30.2677}{516.534}$ gm

= 3.5195 gm.

Amount of Carbon required in the mixture = $24.02 \times \frac{30.2677}{516.534}$ gm

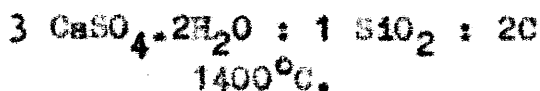
= 1.4076 gm.

Weight of CaSO_4 in 1 gm pellet = $\frac{408.438}{600.614}$

= 0.6800 gm.

Table 8.1.9.

System II.



Weights gm	Time	H_2SO_4 tit-	Sulphide tit-	
		ration	ration	
		cc 0.1 N NaOH used	cc N ₂ /20 KBrO ₃ used	cc N ₂ /100 KBrO ₃ used
Wt. of boat = 6.0566	1mt.	51.0	2.2	
do. + pellet = 6.8315				
Wt. of boat = 6.2099	1mt.	51.0	2.8	
do. + pellet = 6.9919				
Wt. of boat = 6.0388	5 mts.	66.2		0.15
do. + pellet = 6.9065				

Table 8.1.9. (cont'd).
System II.

Weights gm	Time	H ₂ SO ₄ tit- ration	Sulphide tit- ration	
		cc 0.1 N NaOH used	cc N/20 KBrO ₃ used	cc N/100 KBrO ₃ used
Wt. of boat = 5.2622	5 min.	60.9		0.15
do. + pellet = 6.6598				
Wt. of boat = 5.9907	10 "	61.45		0.1
do. + pellet = 6.7808				
Wt. of boat = 6.0180	10 "	61.4		nil
do. + pellet = 6.8075				
Wt. of boat = 5.7960	20 "	59.9		nil
do. + pellet = 6.5217				
Wt. of boat = 5.8836	20 "	63.8		nil
do. + pellet = 6.6687				
Wt. of boat = 6.0556	30 "	66.85		nil
do. + pellet = 6.8521				
Wt. of boat = 6.2088	30 "	66.3		nil
do. + pellet = 6.9761				
Wt. of boat = 6.0553	1 hr.	64.2		nil
do. + pellet = 6.8279				
Wt. of boat = 6.2117	1 "	64.8		nil
do. + pellet = 6.9414				
Wt. of boat = 5.8973	2 hrs.	75.9		nil
do. + pellet = 6.6803				

Table 8.1.9. (cont'd)
System II.

Weights gm	Time	H ₂ SO ₄ tit-	Sulphide tit-	
		ration	ration	
		cc 0.1 N	cc N/20	cc N/100
		NaOH used	KBrO ₃ used	KBrO ₃ used
Wt. of boat = 6.0356	2hrs.	74.4		nil
do. + pellet= 6.8153				
Wt. of boat = 5.8589	3 "	82.3		nil
do. + pellet= 6.7082				
Wt. of boat = 5.8844	3 "	74.45		nil
do. + pellet= 6.6532				

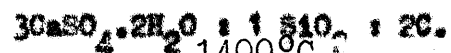
Observations:-

The pellets exfoliated after heating for 1 minute. This exfoliation was always apparent in all systems to follow, where twice the molar amounts of coke or coal was used. Good sinters were obtained in the boats, for higher time intervals. These systems were easy to remove with the help of the stainless steel scaler.

An experiment was performed to note the effect of the increase in the weight of pellet, on desulfurisation. Two pellets of unequal weights were heated for 20 minutes at 1400°C. It was found that 75.32% increase in weight resulted in 9.647% decrease in desulfurisation.

Table 8.1.10.

System II.



Weight of CaSO_4 in 1 gm. pellet = 0.68 gm.

Time	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)	Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
1 mt.	0.7749	0.5269	0.3472	65.895	0.003968	0.753
1 "	0.7820	0.5316	0.3472	65.288	0.005051	0.950
5 "	0.8677	0.5900	0.4507	76.390	0.00005412	0.0192
5 "	0.7976	0.5424	0.4146	76.438	0.00003608	0.0067
10 "	0.7901	0.5373	0.4184	77.871	nil	nil
10 "	0.7895	0.5369	0.4180	77.854	nil	nil
20 "	0.7257	0.4935	0.4078	82.634	nil	nil
20 "	0.7851	0.5339	0.4344	81.364	nil	nil
30 "	0.7965	0.5416	0.4551	84.029	nil	nil
30 "	0.7673	0.5218	0.4514	86.508	nil	nil
1 hr.	0.7726	0.5254	0.4371	83.194	nil	nil
1 hr.	0.7297	0.4962	0.4412	88.916	nil	nil
2 "	0.7830	0.5324	0.5168	97.070	nil	nil

Table 8.1.10 (cont'd)
System II.

Time	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)	% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
2 hrs.	0.7797	0.5302	0.5065	95.530	nil	nil
3 "	0.8493	0.5775	0.5603	97.022	nil	nil
3 "	0.7688	0.5220	0.5069	96.959	nil	nil

SYSTEM I. $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ C. } \circ$

SYSTEM II. $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 2\text{C. } \triangle$

1400°C.

(Oxidising Atmosphere)

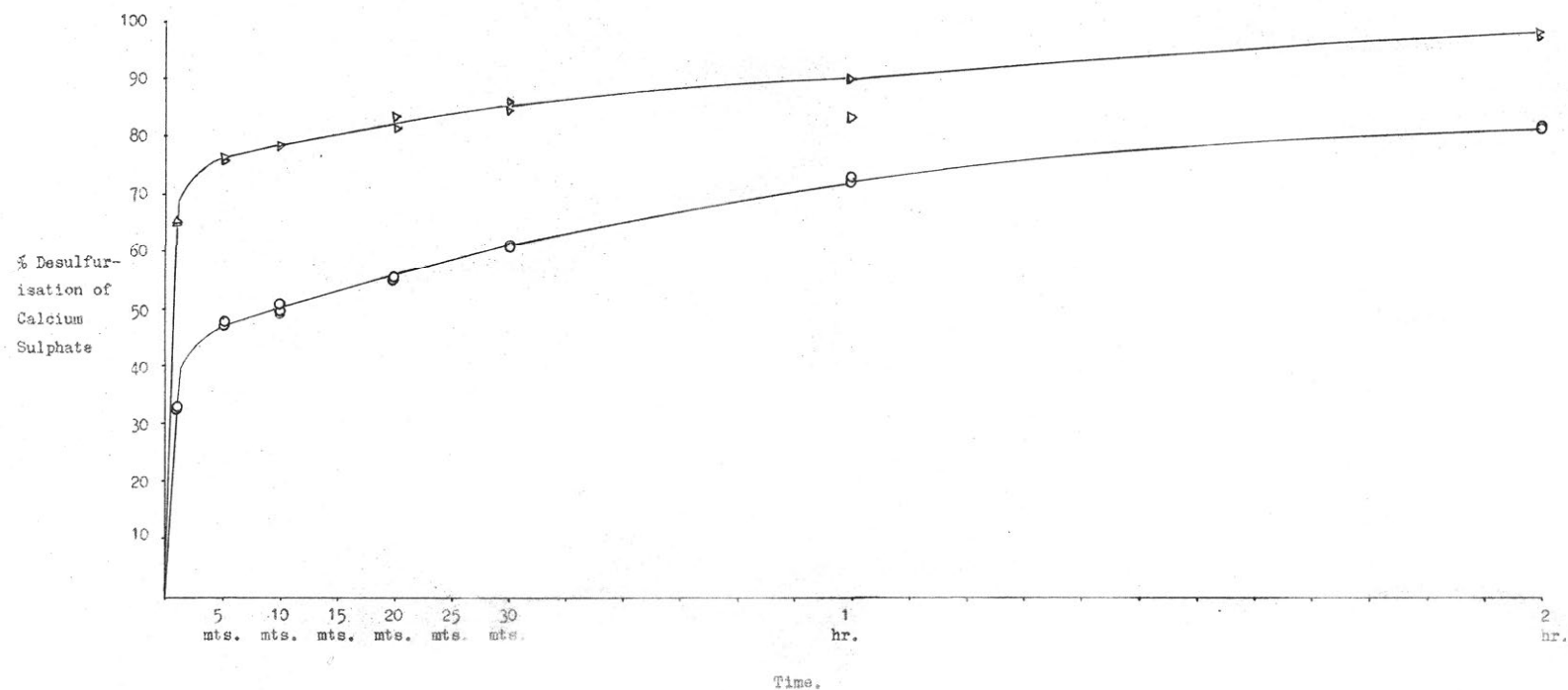
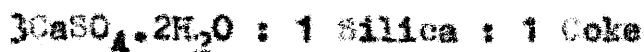


Fig. 8.1,2

System III.



Weight of $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ taken = 32.6744

$$\begin{aligned} \text{Amount of SiO}_2 \text{ required in the mixture} &= 60.06 \times \frac{32.6744}{516.534} \text{ gm} \\ &= 3.7994 \text{ gm.} \end{aligned}$$

Actual amount of carbon in the coke
according to the analysis given in
Appendix I

$$\begin{aligned} &= \text{fixed carbon} - \\ &\quad \text{Total sulphur} \\ &= 67.2 - 6.3 = 60.9\% \end{aligned}$$

This neglect the small percentage of sulphur in the coke
ash and any sulphur in its volatile matter.

$$\text{Corrected ratio of coke} = \frac{100}{60.9} \times 12.01 = 19.721$$

$$\begin{aligned} \text{Amount of coke required in the mixture} &= 19.721 \times \frac{32.6744}{516.534} \text{ gm} \\ &= 1.2476 \text{ gm.} \end{aligned}$$

$$\begin{aligned} \text{Weight of CaSO}_4 \text{ in 1 gm pellet} &= \frac{408.438}{596.315} \times 1 \\ &= 0.6849 \text{ gm.} \end{aligned}$$

$$\text{Weight of coke in 1 gm pellet} = \frac{19.721}{596.315} \times 1 = 0.0331 \text{ gm.}$$

$$\begin{aligned} \text{Weight of S in 1 gm pellet} &= 0.0331 \times \frac{6.3}{100} \text{ gm} \\ &= 0.002085 \text{ gm.} \end{aligned}$$

$$\begin{aligned} \therefore \text{CaSO}_4 \text{ equivalent to weight of S contained in coke} \\ \text{in 1 gm pellet} &= 0.002085 \times \frac{136.146}{32.06} \text{ gm.} \\ &= 0.008854 \text{ gm.} \end{aligned}$$

Table 8.1.11

System III.

$$3 \text{ CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ Coke.}$$

$$1400^\circ\text{C.}$$

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1N NaOH used	Sulphide tit- ration cc N/100 KBrO ₃ used
Wt. of boat = 6.0563	1	40.5	3.0
do. + pellet= 6.8441			
Wt. of boat = 6.2089	1	42.4	5.0
do. + pellet= 7.0702			
Wt. of boat = 5.9033	5	49.9	nil
do. + pellet= 6.7613			
Wt. of boat = 6.9406	5	50.3	nil
do. + pellet= 6.9086			
Wt. of boat = 5.8649	10	52.85	nil
do. + pellet= 6.7550			
Wt. of boat = 6.0081	10	48.7	nil
do. + pellet= 6.7830			
Wt. of boat = 5.9922	20	57.6	nil
do. + pellet= 6.8747			
Wt. of boat = 5.7982	20	56.1	nil
do. + pellet= 6.6850			

Observations:-

Pink melts were obtained after heating for 5 minutes and over. The pink colour was due to the coke ash.

Table 8.1.12.

System III.

 $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 1 \text{ Coke}$

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.6849 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.008854 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulphurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	0.7878	0.5396	0.2757	0.0070	0.2687	49.796	0.001082	0.201
1	0.8613	0.5899	0.2887	0.0076	0.2811	47.652	0.001804	0.306
5	0.8580	0.5876	0.3397	0.0076	0.3321	56.518	nil	nil
5	0.8680	0.5945	0.3425	0.0077	0.3348	56.316	nil	nil
10	0.8901	0.6096	0.3666	0.0079	0.3587	58.842	nil	nil
10	0.7749	0.5307	0.3316	0.0069	0.3247	61.183	nil	nil
20	0.8825	0.6044	0.3922	0.0078	0.3844	63.600	nil	nil
20	0.8868	0.6074	0.3820	0.0079	0.3741	61.590	nil	nil

SYSTEM III.

3 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: 1 Silica : 1 Coke

1400°C.

(Oxidising Atmosphere)

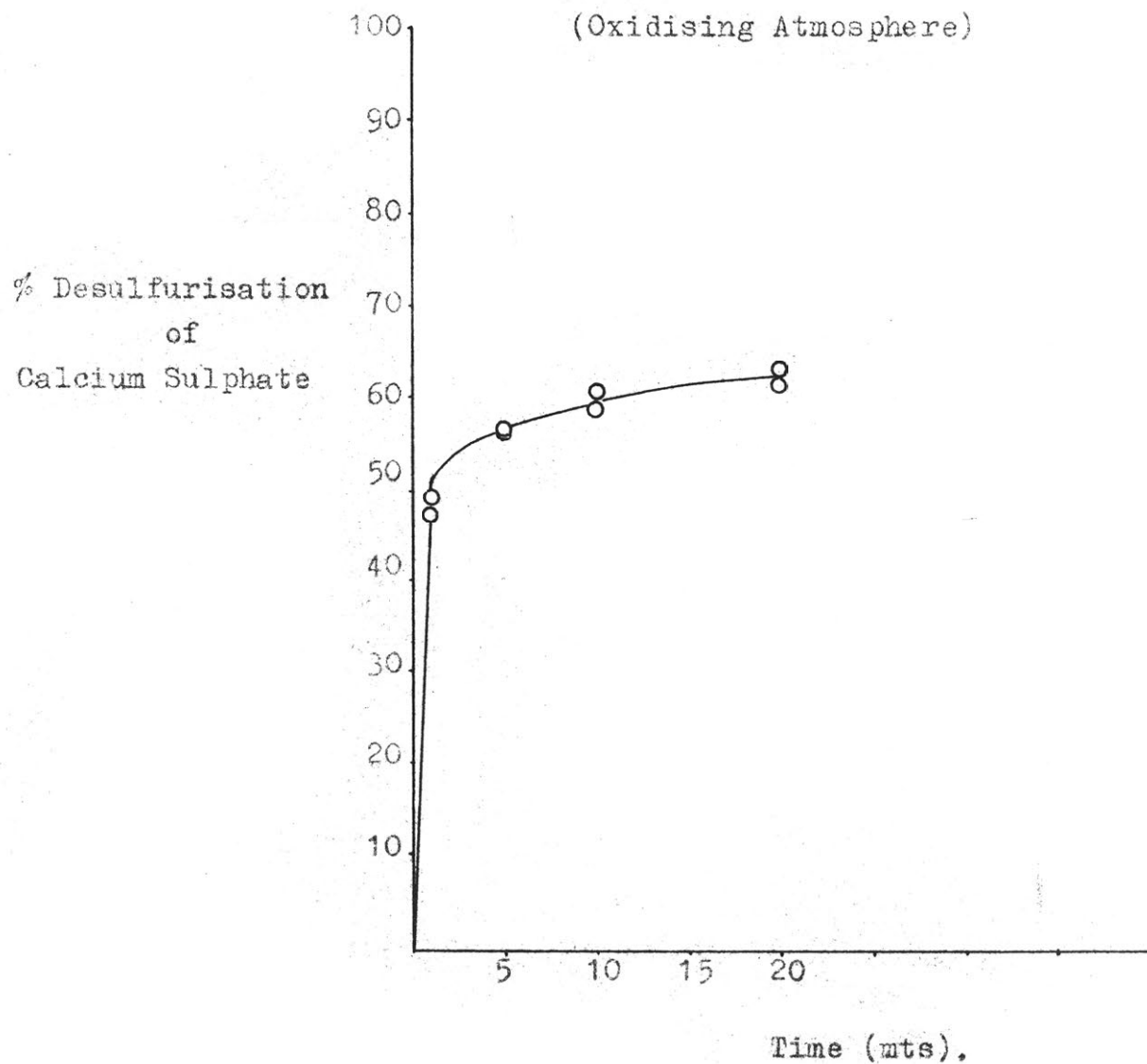


Fig. 8.1.3

System IV.

$$3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 2 \text{ Coke}$$

Weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ taken = 36.5697 gm.

Amount of silica required in the mixture = $\frac{60.06}{516.534} \times 36.5697 \text{ gm}$
 = 4.2521 gm.

Corrected ratio of coke = $\frac{100}{60.9} \times 24.02 = 39.442$

Amount of Coke required in the mixture = $\frac{39.442}{516.534} \times 36.5697 \text{ gm}$
 = 2.7924 gm.

Weight of CaSO_4 in 1 gm pellet = $\frac{408.438}{616.036} \times 1$
 = 0.663 gm

Weight of coke in 1 gm pellet = $\frac{39.442}{616.036} \times 1 = 0.064 \text{ gm.}$

Weight of S in 1 gm pellet = $0.064 \times \frac{6.3}{100} = 0.004032 \text{ gm.}$

∴ CaSO_4 equivalent to the above weight

of S contained in coke in 1 gm pellet = $0.004032 \times \frac{136.146}{32.06}$
 = 0.01712 gm.

Table 8.1.13.

System IV.



Weights gm	Time (mts)	H ₂ NO ₄ tit- ration	Sulphide tit- ration	
		cc 0.1N NaOH used	cc N/20 KBrO ₃ used	cc N/100 KBrO ₃ used
Wt. of boat = 6.2084	1	37.2	21.6	
do. + pellet= 6.9584				
Wt. of boat = 5.9066	1	37.4	19.8	
do. + pellet= 6.6666				
Wt. of boat = 5.8684	5	63.9		0.25
do. + pellet= 6.6458				
Wt. of boat = 6.0099	5	60.35		0.2
do. + pellet= 6.7582				
Wt. of boat = 6.0010	10	75.6		nil
do. + pellet= 6.9083				
Wt. of boat = 6.0265	10	63.3		nil
do. + pellet= 6.7931				
Wt. of boat = 5.8064	20	69.45		nil
do. + pellet= 6.6269				
Wt. of boat = 5.8876	20	66.7		nil
do. + pellet= 6.6759				

Observations:-

By using 2 moles of coke, the melts were completely avoided. The pellets on heating, first exfoliated and then sintered. The colour change on

heating was from buff to dark brown with increase in the time of heating. Owing to the presence of Fe_2O_3 in coke ash, the boats were stained blue, due to the formation of iron-platinum alloy.

Table 8.1.14.

System IV.

Weight of CaSO_4 in 1 gm pellet = 0.663 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.01712 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)		% Desulfurised CaSO_4		Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO ₄ equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	0.7500	0.4973	0.2533	0.0128	0.2405	48.361	0.03896	7.834
1	0.7600	0.5039	0.2546	0.0130	0.2416	47.946	0.03572	7.088
5	0.7774	0.5154	0.4351	0.0133	0.4218	81.8393	0.00009019	0.0175
5	0.7483	0.4961	0.4109	0.0128	0.3981	80.246	0.00007215	0.0145
10	0.9073	0.6015	0.5147	0.0155	0.4992	82.993	nil	nil
10	0.7666	0.5083	0.4310	0.0131	0.4179	82.215	nil	nil
20	0.8205	0.5440	0.4728	0.0140	0.4588	84.338	nil	nil
20	0.7883	0.5226	0.4541	0.0135	0.4406	84.309	nil	nil

System V.

3 Gypsum : 1 Silica : 2 Coke.

The mineral gypsum being reasonably pure, was substituted for synthetic $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in order to note any change in desulfurisation.

Weight of Gypsum taken = 37.4043 gm.

$$\begin{aligned} \therefore \text{Amount of silica required in the mixture} &= 60.06 \times \frac{37.4043}{516.534} \text{ gm} \\ &= 4.3483 \text{ gm.} \end{aligned}$$

$$\text{Corrected ratio of coke} = \frac{100}{60.9} \times 24.02 = 39.442$$

$$\begin{aligned} \therefore \text{Amount of coke required in the mixture} &= 39.442 \times \frac{37.4043}{516.534} \text{ gm} \\ &= 2.8556 \text{ gm.} \end{aligned}$$

$$\text{Weight of } \text{CaSO}_4 \text{ in 1 gm pellet} = \frac{408.438}{616.036} \times 1 = 0.663 \text{ gm}$$

$$\text{Weight of coke in 1 gm pellet} = \frac{39.442}{616.036} \times 1 = 0.0640 \text{ gm}$$

$$\therefore \text{Weight of S in 1 gm pellet} = 0.064 \times \frac{6.3}{100} = 0.004032 \text{ gm.}$$

$$\begin{aligned} \therefore \text{CaSO}_4 \text{ equivalent to weight of S} \\ \text{contained in coke in 1 gm pellet} &= 0.004032 \times \frac{136.146}{32.06} \\ &= 0.01712 \text{ gm.} \end{aligned}$$

Table 8.1.15.

System V.

3 Gypsum : 1 Silica : 2 Coke

1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration	Sulphide titra- tion	
		cc 0.1N NaOH used	cc N/20 KBrO ₃ used	cc N/100 KBrO ₃ used
Wt. of boat = 6.2098	1	52.95	20.0	
do. + pellet= 7.1565				
Wt. of boat = 5.8047	1	51.35	21.5	
do. + pellet= 6.8302				
Wt. of boat = 6.0443	5	76.9		0.1
do. + pellet= 6.9912				
Wt. of boat = 5.8678	5	80.45		0.15
do. + pellet= 6.8595				
Wt. of boat = 5.9968	10	79.25		nil
do. + pellet= 6.9614				
Wt. of boat = 6.0226	10	81.0		nil
do. + pellet= 7.0109				
Wt. of boat = 5.8923	20	81.4		nil
do. + pellet= 6.7588				
Wt. of boat = 5.8851	20	79.0		nil
do. + pellet= 6.8159				

Observations:-

The condition and colour of the pellets was the same as in System IV.

Table 8.1.16.

System V.

3 Gypsum : 1 Silica : 2 Coke.
1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.663 gm.

CaSO_4 equivalent to the wt. of S. contained in coke in 1 gm pellet = 0.01712 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	0.9467	0.6277	0.3605	0.0162	0.3443	54.851	0.03608	5.748
1	0.9255	0.6136	0.3496	0.0158	0.3338	54.400	0.03878	6.320
5	0.9469	0.6278	0.5236	0.0162	0.5074	80.822	0.00003608	0.00575
5	0.9917	0.6575	0.5477	0.0170	0.5307	80.715	0.00005412	0.00823
10	0.9646	0.6395	0.5396	0.0165	0.5231	81.798	nil	nil
10	0.9883	0.6552	0.5515	0.0169	0.5346	81.593	nil	nil
20	0.9565	0.6342	0.5542	0.0164	0.5378	84.800	nil	nil
20	0.9308	0.6171	0.5379	0.0159	0.5220	84.569	nil	nil

SYSTEM V. 3 Gypsum : 1 Silica : 2 Coke
1400°C.
(Oxidising Atmosphere)

Δ

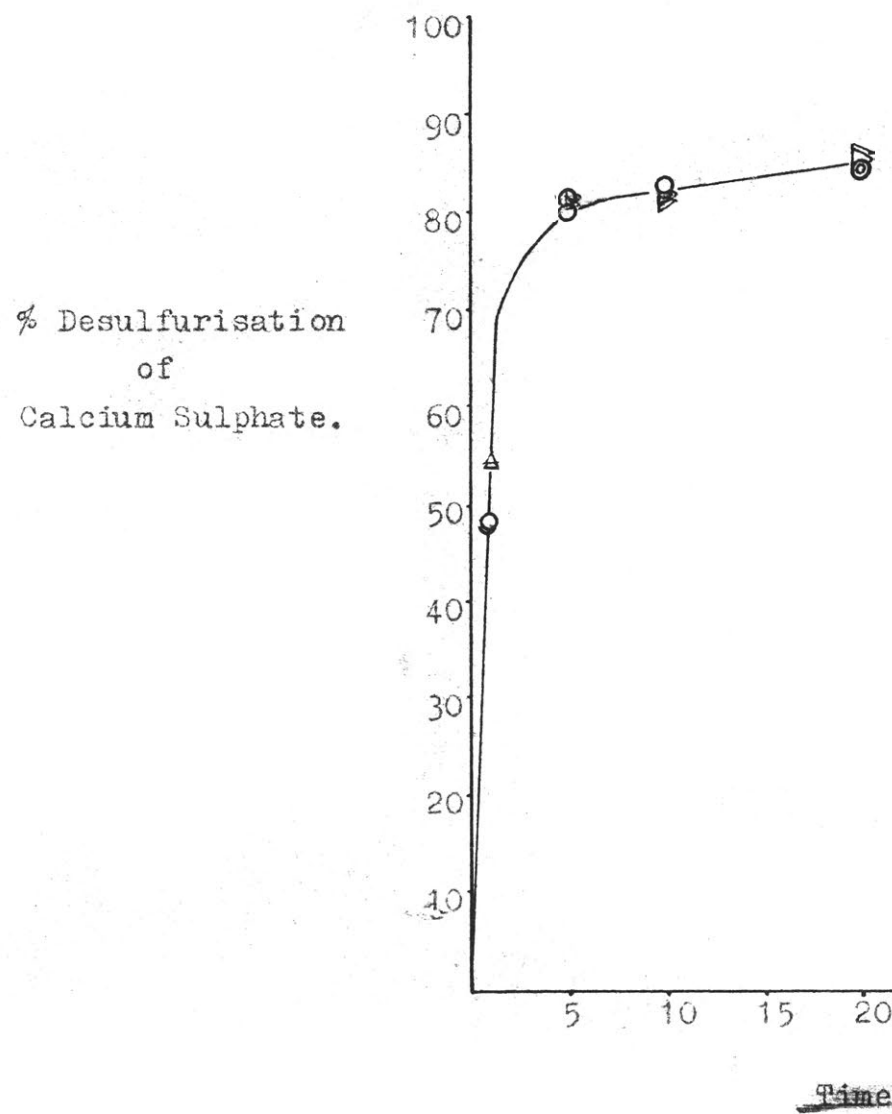


Fig. 8.1.4

System VI.



Calculation of the actual amount of carbon in the coal according to the analysis given in

Appendix I:-

If 67.2 parts of fixed carbon in the char include 6.3 parts of sulphur, then 36.9 parts of fixed carbon will contain = $\frac{36.9 \times 6.3}{67.2}$ = 3.46 parts of S.

67.2

Sulphur free fixed-carbon in coal = $36.9 - 3.46$
= 33.44%

This neglects the small percentage of sulphur in the coke ash and any sulphur in the volatile matter of coke.

Weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ taken = 38.1053 gm.

Corrected ratio of coal = $\frac{100}{33.44} \times 24.02$ = 71.83

Amount of Silica required in the mixture = $60.06 \times \frac{38.1053}{516.534}$ gm.
= 4.4306 gm.

Amount of coal required in the mixture = $71.83 \times \frac{38.1053}{516.534}$ gm.
= 5.2989 gm.

Weight of CaSO_4 in 1 gm pellet = $\frac{408.438}{648.424} \times 1$ = 0.6299 gm.

Weight of coal in 1 gm pellet = $\frac{71.83}{648.424} \times 1$ = 0.1108 gm.

∴ Weight of S in 1 gm pellet = $0.1108 \times \frac{6.7}{100}$ = 0.007424 gm.

∴ CaSO_4 equivalent to the above weight of S contained in coal in 1 gm pellet = $0.007424 \times \frac{136.146}{32.06}$ gm.
= 0.03153 gm.

Table 8.1.17

System VI.

$3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 2 \text{ Coal}$
 1400°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc 0.1N NaOH used	Sulphide titra- tion	
			cc N/20 KBrO_3 used	cc N/100 KBrO_3 used
Wt. of boat = 6.0555	1	25.6	65.4	
do. + pellet= 6.8922				
Wt. of boat = 6.2088	1	27.3	64.3	
do. + pellet= 7.0070				
Wt. of boat = 5.9070	5	63.6		3.2
do. + pellet= 6.7730				
Wt. of boat = 6.0439	5	62.5		3.1
do. + pellet= 6.8968				
Wt. of boat = 5.8716	10	60.5		nil
do. + pellet= 6.6845				
Wt. of boat = 6.0134	10	61.0		nil
do. + pellet= 6.8082				
Wt. of boat = 6.0357	20	60.8		nil
do. + pellet= 6.8142				
Wt. of boat = 5.8877	20	59.8		nil
do. + pellet= 6.6741				

Observations:-

Vigorous evolution of volatiles containing sulfur dioxide took place when coal was used as a

constituent, of the system. Some heavier hydrocarbons accumulated near the cooler ends of the reactor and were removed constantly. The pellets got exfoliated and changed in colour from light buff to brown with increasing time intervals.

Table E.1.18.

System VI.

 $3 \text{ CaSO}_4 \cdot 2\text{H}_2\text{O} : 1 \text{ Silica} : 2 \text{ Coal}$

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.5299 gm. CaSO_4 equivalent to the wt. of S contained in coal in 1 gm pellet = 0.03153 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Resulfurised CaSO_4 (gm)			% Resulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coal (b)	Correct- ed (a-b)			
1	0.8367	0.5270	0.1743	0.0264	0.1479	28.065	0.1180	22.391
1	0.7982	0.5028	0.1859	0.0252	0.1607	31.961	0.1160	23.071
5	0.8660	0.5455	0.4330	0.0273	0.4057	74.372	0.001154	0.212
5	0.8529	0.5372	0.4255	0.0269	0.3986	74.200	0.001118	0.131
10	0.8123	0.5120	0.4113	0.0256	0.3863	75.449	nil	nil
10	0.7948	0.5006	0.4153	0.0251	0.3902	77.946	nil	nil
20	0.7785	0.4904	0.4140	0.0245	0.3895	79.425	nil	nil
20	0.7864	0.4954	0.4071	0.0248	0.3823	77.170	nil	nil

System VII.

3 Gypsum : 1 Silica : 2 Coal

Weight of gypsum taken = 35.0122 gm.

Corrected ratio of coal = $\frac{100}{33.43} \times 24.02 = 71.83$ Amount of silica required in the mixture = $60.06 \times \frac{35.0122 \text{ gm}}{516.534}$

= 4.0709 gm.

Amount of coal required in the mixture = $71.83 \times \frac{35.0122 \text{ gm}}{516.534}$

= 4.8686 gm.

Weight of CaSO_4 in 1 gm pellet = $\frac{408.438}{648.424} \times 1$
= 0.6299 gm.Weight of coal in 1 gm pellet = $\frac{71.83}{648.424} \times 1 = 0.1108 \text{ gm.}$ Weight of S in 1 gm pellet = $0.1108 \times \frac{6.7}{100}$
= 0.007424 gm.∴ CaSO_4 equivalent to the above weightof S contained in coal in 1 gm pellet = $0.007424 \times \frac{136.146 \text{ gm}}{32.06}$

= 0.03153 gm.

Table 8.1.19

System VII.

3 Gypsum : 1 Silica : 2 Coal

1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1 N	Sulphide titration	
			cc N/20 KBrO ₃ used	cc N/100 KBrO ₃ used
Wt. of boat = 6.2088	1	26.2	70.9	
do. + pellet= 7.2174				
Wt. of boat = 5.9070	1	26.8	71.4	
do. + pellet= 6.9225				
Wt. of boat = 6.0453	5	69.7		3.5
do. + pellet= 7.0672				
Wt. of boat = 5.8710	5	71.85		3.7
do. + pellet= 6.9343				
Wt. of boat = 6.0125	10	68.85		nil
do. + pellet= 7.0130				
Wt. of boat = 6.0024	10	74.9		nil
do. + pellet= 7.0764				
Wt. of boat = 6.0366	20	71.55		nil
do. + pellet= 7.0256				
Wt. of boat = 5.8079	20	71.1		nil
do. + pellet= 6.7861				

Observations:-

Same as in System VI.

Table 8.1.20.

System VII.

3 Gypsum : 1 Silica : 2 Coal.

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.6299 gm. CaSO_4 equivalent to the wt. of S contained in coal in 1 gm pellet = 0.03153 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coal (b)	Correct- ed (a-b)			
1	1.0086	0.6352	0.1784	0.0318	0.1466	23.076	0.1279	20.132
1	1.0155	0.6397	0.1825	0.0320	0.1505	23.527	0.1288	20.134
5	1.0219	0.6437	0.4745	0.0322	0.4423	68.712	0.001263	0.196
5	1.0633	0.6698	0.4892	0.0335	0.4557	68.0352	0.001335	0.199
10	1.0005	0.6302	0.4688	0.0315	0.4373	69.391	nil	nil
10	1.0740	0.6765	0.5099	0.0339	0.4760	70.362	nil	nil
20	0.9890	0.6230	0.4871	0.0312	0.4559	73.178	nil	nil
20	0.9782	0.6162	0.4841	0.0308	0.4533	73.564	nil	nil

1400°C.
(Oxidising Atmosphere)

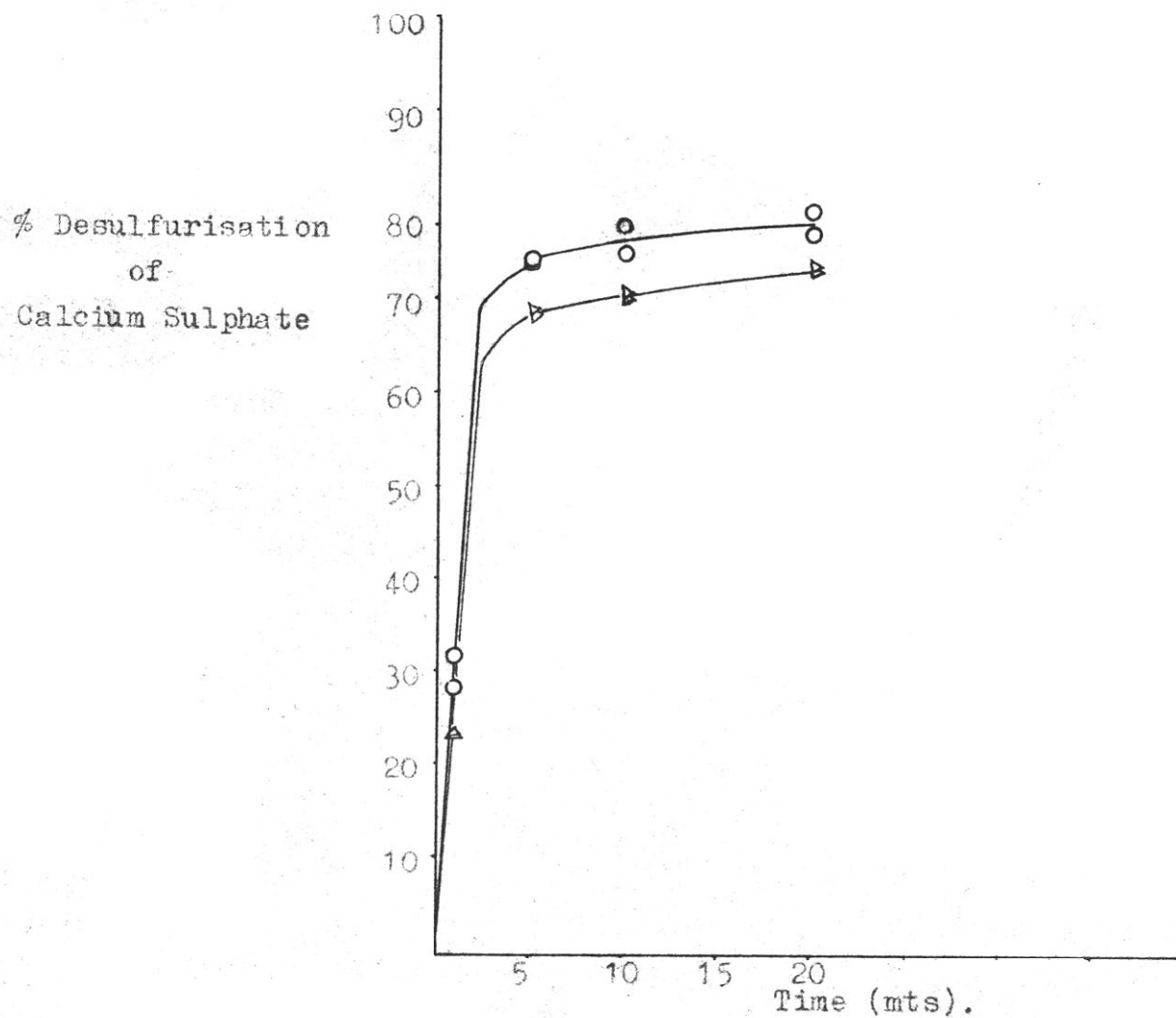


Fig. 8.1.5

System VIII.

3 Gypsum : 1 Silica.

Weight of gypsum taken = 32.6847 gm.

Amount of silica required in the mixture = $60.06 \times \frac{32.6847}{516.534}$ gm

= 3.8001 gm.

Weight of CaSO_4 in 1 gm pellet = $\frac{408.438}{576.594} \times 1$

= 0.7084 gm.

Table 8.1.21.
 System VIII.
 3 Gypsum : 1 Silica.
 1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ titration cc 0.1 N NaOH used
Wt. of boat = 6.0441	1	6.35
do. + pellet= 7.0366		
Wt. of boat = 6.0243	1	6.2
do. + pellet= 6.9937		
Wt. of boat = 5.8552	5	37.9
do. + pellet= 6.8141		
Wt. of boat = 6.0965	5	39.85
do. + pellet= 7.1150		
Wt. of boat = 5.9777	10	43.9
do. + pellet= 6.9127		
Wt. of boat = 5.8765	10	44.8
do. + pellet= 6.8441		
Wt. of boat = 6.0125	20	48.55
do. + pellet= 6.9639		
Wt. of boat = 5.8904	20	49.5
do. + pellet= 6.8450		

Observations:-

White melts were obtained, which spread along the sides of the boats.

Table 8.1.22.

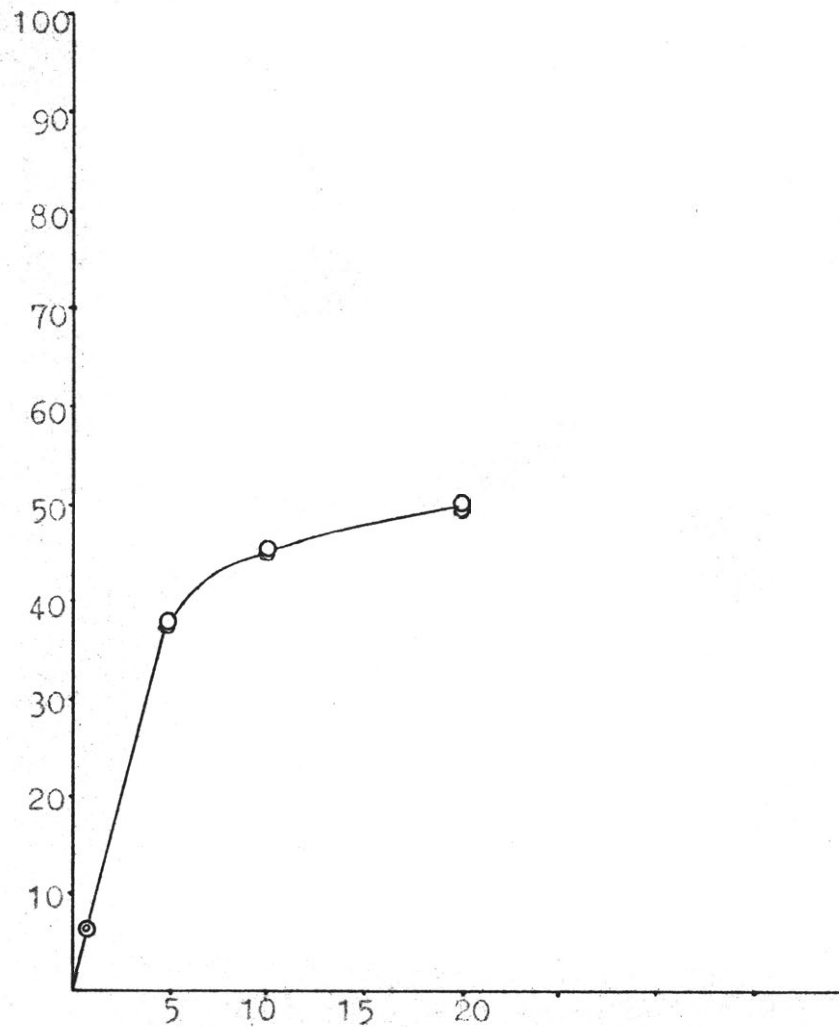
System VIII.

3 Gypsum : 1 SiO_2 .Weight of CaSO_4 in 1 gm pellet = 0.7084 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)	% Desulfurised CaSO_4
1	0.9925	0.7031	0.0432	6.144
1	0.9694	0.6867	0.0422	6.145
5	0.9589	0.6793	0.2580	37.980
5	1.0185	0.7215	0.2713	37.602
10	0.9350	0.6624	0.2989	45.124
10	0.9676	0.6854	0.3050	44.500
20	0.9514	0.6740	0.3305	49.036
20	0.9546	0.6762	0.3370	49.837

1400°C
(Oxidising Atmosphere)

% Desulfurisation
of
Calcium Sulphate



Time (mts).

Fig. 8.1.6

System IX.

3 Gypsum : 2 Coal.

Weight of gypsum taken = 45.7153 gm.

$$\text{Corrected ratio of coal} = \frac{100}{33.44} \times 24.02 = 71.83$$

$$\therefore \text{Amount of coal required in the mixture} = 71.83 \times \frac{45.7153 \text{ gm}}{516.534}$$

$$= 6.3572 \text{ gm.}$$

$$\text{Weight of CaSO}_4 \text{ in 1 gm pellet} = \frac{408.438}{588.364} \times 1$$

$$= 0.6942 \text{ gm.}$$

$$\text{Weight of coal in 1 gm pellet} = \frac{71.83}{588.364} \times 1$$

$$= 0.1221 \text{ gm.}$$

$$\therefore \text{Weight of S in 1 gm pellet} = 0.1221 \times \frac{6.7}{100}$$

$$= 0.008181 \text{ gm.}$$

$$\therefore \text{CaSO}_4 \text{ equivalent to the above}$$

$$\text{weight of S contained in coal in}$$

$$1 \text{ gm pellet} = 0.008181 \times \frac{136.146}{32.06} \text{ gm}$$

$$= 0.03474 \text{ gm.}$$

Table 8.1.23.

System IX.

3 Gypsum : 2 Coal.

1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1 N NaOH used	Sulphide titration	
			cc N/20	cc N/100
			KBrO ₃ used	KBrO ₃ used
Wt. of boat = 6.0567	1	27.4	90.6	
do. + pellet= 7.0563				
Wt. of boat = 6.0431	1	26.5	101.6	
do. + pellet= 7.0545				
Wt. of boat = 5.8690	5	68.3		7.9
do. + pellet= 6.8190				
Wt. of boat = 6.0103	5	72.0		8.9
do. + pellet= 7.0047				
Wt. of boat = 6.0015	10	68.05		nil
do. + pellet= 6.9215				
Wt. of boat = 5.8061	10	70.95		nil
do. + pellet= 6.7670				
Wt. of boat = 5.8862	20	73.3		nil
do. + pellet= 6.8248				
Wt. of boat = 5.9070	20	76.15		nil
do. + pellet= 6.8958				

Observations:-

Same as in System VI.

Table 8.1.24.

System IX.

3 Gypm. to 2 Coal.

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.6942 gm. CaSO_4 equivalent to the wt. of S contained in coal in 1 gm pellet = 0.03474 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coal (b)	Correct- ed (a-b)			
1	0.9996	0.6939	0.1866	0.0347	0.1519	21.891	0.1634	23.548
1	1.0114	0.7021	0.1804	0.0351	0.1453	20.695	0.1833	26.107
5	0.9500	0.6595	0.4650	0.0330	0.4320	65.504	0.00285	0.432
5	0.9944	0.6903	0.4902	0.0345	0.4557	66.0148	0.00321	0.465
10	0.9200	0.6387	0.4633	0.0320	0.4313	67.528	nil	nil
10	0.9609	0.6671	0.4831	0.0334	0.4497	67.411	nil	nil
20	0.9386	0.6516	0.4991	0.0326	0.4665	71.593	nil	nil
20	0.9888	0.6864	0.5185	0.0344	0.4841	70.527	nil	nil

System X.

3 Gypsum : 2 Coke.

Weight of gypsum taken = 32.8 gm.

Corrected ratio of coke = $\frac{100}{60.9} \times 24.02 = 39.442 \text{ gm.}$ Amount of coke required in the mixture = $39.442 \times \frac{32.8}{516.534} \text{ gm.}$

= 2.5046 gm.

Weight of CaSO_4 in 1 gm pellet = $\frac{408.438}{555.976} \times 1 \text{ gm}$

= 0.7346 gm.

Weight of coke in 1 gm pellet = $\frac{39.442}{555.976} \times 1$

= 0.07094 gm.

Weight of S in 1 gm pellet = $0.07094 \times \frac{6.3}{100}$

= 0.004469 gm.

∴ CaSO_4 equivalent to the weight
of S contained in coke in 1 gm
pellet

= $0.004469 \times \frac{136.146}{32.06}$

= 0.01898 gm.

System X.
3 Gypsum : 2 Coke.
1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1N NaOH used	Sulphide titration	
			cc N/20 KBrO ₃ used	cc N/100 KBrO ₃ used
Wt. of boat = 6.0563	1	43.85	32.0	
do. + pellet= 7.0301				
Wt. of boat = 6.2096	1	43.7	35.2	
do. + pellet= 7.1954				
Wt. of boat = 5.9063	5	72.25		0.3
do. + pellet= 6.8276				
Wt. of boat = 6.0433	5	72.65		0.3
do. + pellet= 6.9662				
Wt. of boat = 5.8683	10	77.3		nil
do. + pellet= 6.8249				
Wt. of boat = 6.0093	10	77.3		nil
do. + pellet= 6.9706				
Wt. of boat = 6.0015	20	81.6		nil
do. + pellet= 6.9750				
Wt. of boat = 6.0248	20	80.55		nil
do. + pellet= 6.9810				

Observations:-

Pellets were less exfoliated when coke was present as compared to coal. Similarly evolution of gases was also less brisk. With increase in the duration of heating, the colour changed, from buff to dark brown.

Table 8.1.26.

System X.

3 Gypsum : 2 Coke.

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.7346 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.01898 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO ₄ in pellet (gm)	Weight of Desulfurised			% Desulfurised CaSO ₄	Weight of CaS formed (gm)	% CaS formed
			CaSO ₄ (gm)					
			Total (a)	CaSO ₄ equiv- alent to wt. of S in coke (b)	Correct- ed (a-b)			
1	0.9738	0.7154	0.2985	0.0185	0.2800	39.139	0.05772	8.068
1	0.9858	0.7242	0.2975	0.0187	0.2788	38.498	0.06350	8.768
5	0.9213	0.6768	0.4919	0.0175	0.4744	70.095	0.0001082	0.0160
5	0.9229	0.6780	0.4946	0.0175	0.4771	70.369	0.0001082	0.0160
10	0.9566	0.7027	0.5263	0.0182	0.5081	72.307	nil	nil
10	0.9613	0.7062	0.5263	0.0182	0.5081	71.948	nil	nil
20	0.9735	0.7151	0.5556	0.0185	0.5371	75.108	nil	nil
20	0.9562	0.7024	0.5484	0.0181	0.5303	75.498	nil	nil

SYSTEM X. 3 Gypsum : 2 Coke Δ

1400°C.

(Oxidising Atmosphere)

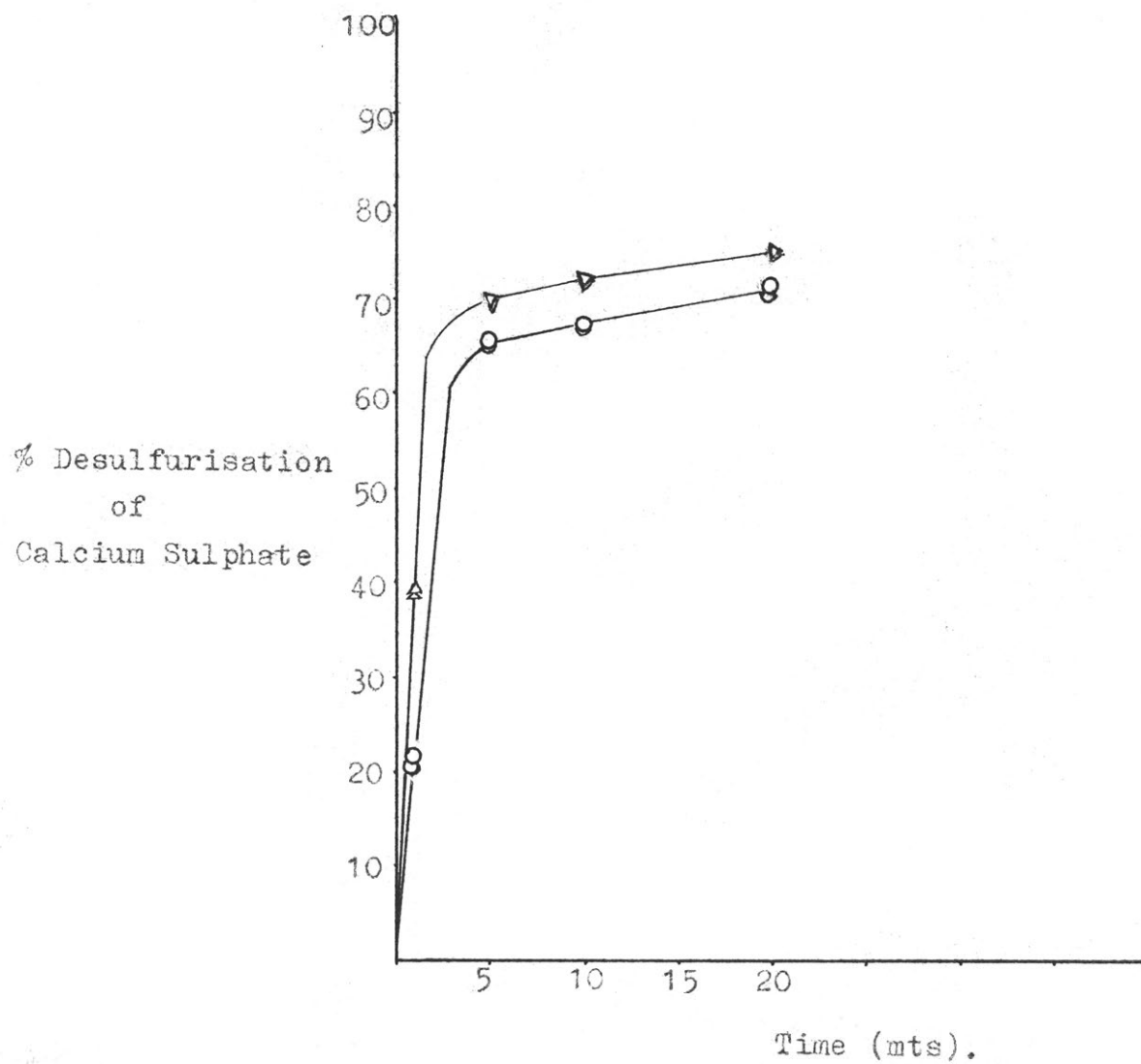


Fig. 8.1.7

Introduction to Systems XI, XII and XIII.

These systems were investigated in order to study the desulfurisation, as well as the cement clinker, formed by the addition of the right amount of Al_2O_3 and Fe_2O_3 to the system: 3 Gypsum : 1 Silica : 2 Coke. In systems XI and XII, Al_2O_3 and Fe_2O_3 were added separately and in system XIII, together.

A.S.T.M. recognises 5 types of Portland cements. Of these Type I is the general use cement, and is employed in general concrete construction, whereas the rest are used for specific purposes only. The percentage by weight of CaO , Al_2O_3 and Fe_2O_3 in Type I Portland cement are as follows (28):-

CaO	Fe_2O_3	Al_2O_3
63.2	2.7	6

The molar ratios of 3 Gypsum : 1 Silica, should theoretically give a cement with maximum amount of tri-calcium silicate, therefore keeping these ratios the same, the amounts of Al_2O_3 and Fe_2O_3 to be added, were calculated on the basis of Type I Portland cement.

Calculations:-

3 gram-molecules of gypsum contain 168.24 grams of CaO

$$\therefore \text{Required weight of } \text{Al}_2\text{O}_3 = \frac{6 \times 168.24}{63.2} = 15.972 \text{ gm}$$

$$\text{do. do. do. } \text{Fe}_2\text{O}_3 = \frac{2.7 \times 168.24}{63.2} = 7.1874 \text{ gm}$$

Expressing these weights as molar ratios:-

$$\text{The molar ratio of } \text{Al}_2\text{O}_3 = \frac{15.972}{101.94} = 0.1567$$

$$\text{do. do. of } \text{Fe}_2\text{O}_3 = \frac{7.1874}{159.68} = 0.04501$$

Therefore the constituents of systems XI, XII and XIII were taken in the following molar ratios, in order to obtain a good clinker.

System XI:- 3 Gypsum : 1 Silica : 2 Coke : 0.1567 Al_2O_3

System XII:- 3 Gypsum : 1 Silica : 2 Coke : 0.04501 Fe_2O_3

System XIII:- 3 Gypsum : 1 Silica : 2 Coke : 0.1567 Al_2O_3 :
0.04501 Fe_2O_3

System XI.

3 Gypsum : 1 SiO_2 : 2 Coke : 0.1567 Al_2O_3 .

Weight of gypsum taken = 35.7143 gm.

$$\therefore \text{Amount of silica required in the mixture} = 60.06 \times \frac{35.7143}{516.534} \text{ gm}$$

$$= 4.1525 \text{ gm.}$$

$$\text{Corrected ratio of coke} = \frac{100}{60.9} \times 24.02 = 39.442$$

$$\therefore \text{Amount of coke required in the mixture} = 39.442 \times \frac{35.7143}{516.534} \text{ gm}$$

$$= 2.7270 \text{ gm.}$$

Amount of ash in coke = 30.2%

" " Alumina in ash = 29.35%

$$\text{Amount of } \text{Al}_2\text{O}_3 \text{ in 1 gm coke} = \frac{30.2}{100} \times 1 \times \frac{29.35}{100} \text{ gm}$$

$$= 0.08864 \text{ gm.}$$

$$\therefore \text{Corrected ratio of } \text{Al}_2\text{O}_3 = 15.972 - (39.442 \times 0.08864) \text{ gm}$$

$$= 12.4759 \text{ gm.}$$

$$\text{Amount of } \text{Al}_2\text{O}_3 \text{ required in the mixture} = 12.4759 \times \frac{35.7143}{516.534} \text{ gm}$$

$$= 0.8626 \text{ gm}$$

$$\text{Weight of } \text{CaSO}_4 \text{ in 1 gm pellet} = \frac{408.438}{516.534 + 60.06 + 39.442 + 12.4759} \times 1 \text{ gm.}$$

$$= 0.6498 \text{ gm.}$$

$$\text{Weight of coke in 1 gm pellet} = \frac{39.442}{628.5119} \times 1 = 0.06275 \text{ gm}$$

$$\therefore \text{Weight of S in 1 gm pellet} = 0.06275 \times \frac{6.3}{100} = 0.003953 \text{ gm}$$

$$\therefore \text{CaSO}_4 \text{ equivalent to wt. of S}$$

$$\text{contained in coke in 1 gm pellet} = 0.003953 \times \frac{136.146}{32.06} \text{ gm}$$

$$= 0.0168 \text{ gm}$$

Table A.1.27.

System XI.

3 Gypsum : 1 Silica : 2 Coke : 0.1567 Al_2O_3 .
 1400°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc 0.1 N NaOH used	Sulphide titration	
			cc N/20 KBrO_3 used	cc N/100 KBrO_3 used
Wt. of boat = 6.2020	1	52.35	24.35	
do. + pellet= 7.1630				
Wt. of boat = 5.8835	1	51.9	20.1	
do. + pellet= 6.8537				
Wt. of boat = 6.0229	5	82.3		nil
do. + pellet= 7.0267				
Wt. of boat = 5.8490	5	81.7		nil
do. + pellet= 6.8415				
Wt. of boat = 6.0889	10	79.5		nil
do. + pellet= 7.0391				
Wt. of boat = 5.7835	10	91.0		nil
do. + pellet= 6.8870				
Wt. of boat = 5.8829	20	81.8		nil
do. + pellet= 6.8604				
Wt. of boat = 6.2024	20	81.6		nil
do. + pellet= 7.1668				

Observations:-

Exfoliation occurred after heating for 1 minute.
 With the rise in the time of heating, shiny slate grey
 sinters were obtained.

Table 8.1.28.

System XI.

3 Gypsum : 1 Silica : 2 Coke : 0.1567 Al_2O_3 .
 1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.6498 gm.

CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.0168 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Desulfurised CaSO_4			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	0.9610	0.6245	0.3564	0.0161	0.3403	54.492	0.04392	7.033
1	0.9702	0.6304	0.3534	0.0163	0.3371	53.474	0.03626	5.752
5	1.0038	0.6523	0.5603	0.0169	0.5434	83.305		
5	0.9926	0.6450	0.5562	0.0167	0.5395	83.643		
10	0.9502	0.6174	0.5413	0.0160	0.5253	85.083		
10	1.1035	0.7171	0.6196	0.0185	0.6011	83.824		
20	0.9775	0.6352	0.5569	0.0164	0.5405	85.091		
20	0.9644	0.6267	0.5556	0.0162	0.5394	86.070		

SYSTEM XI.

3 Gypsum : 1 Silica : 2 Coke: 0.1567 Al_2O_3

1400°C.

(Oxidising Atmosphere).

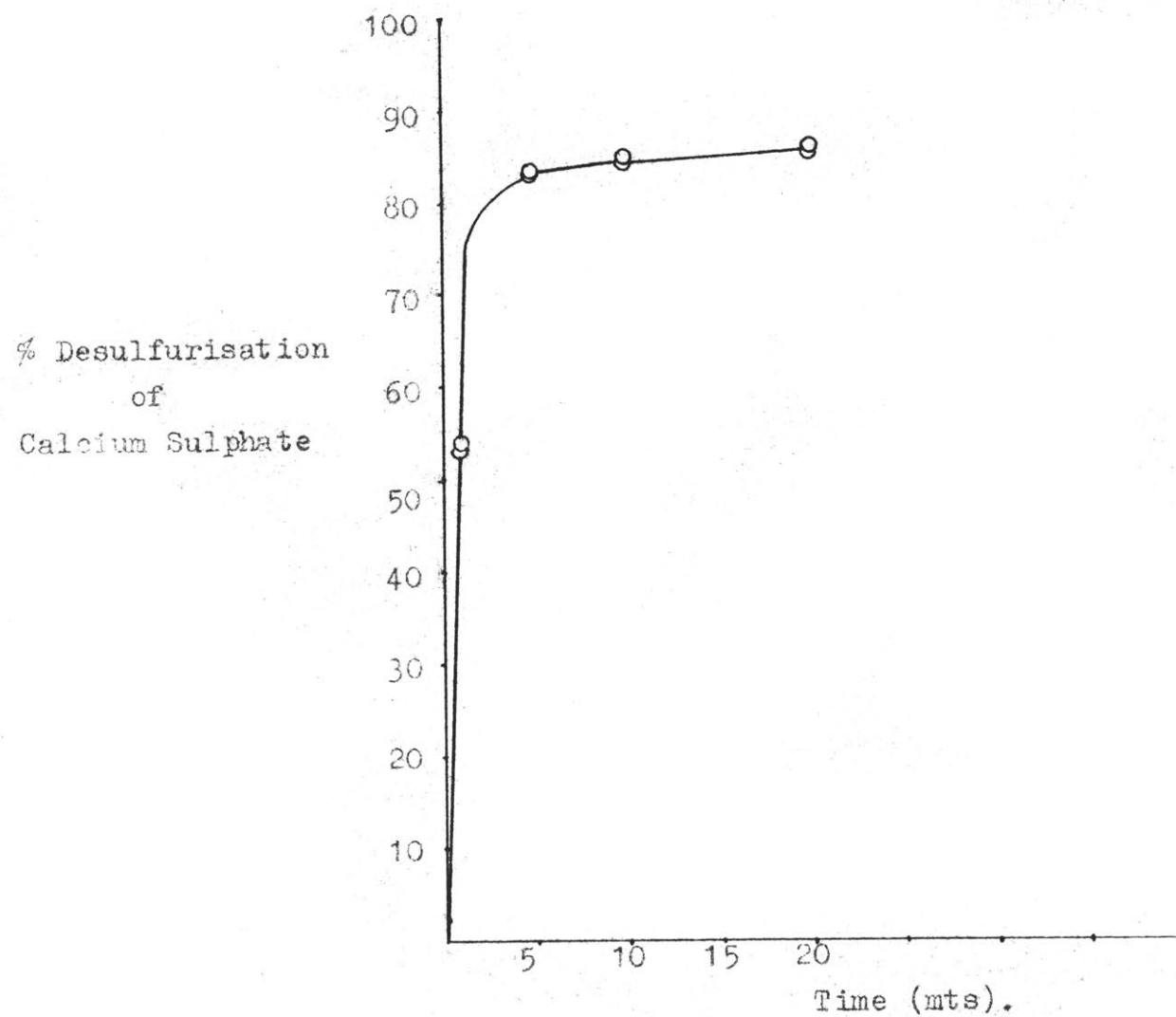


Fig. 8.1.8

System XII.

3 Gypsum : 1 SiO_2 : 2 Coke : 0.04501 Fe_2O_3 .

Weight of gypsum taken = 34.8430 gm.

Amount of SiO_2 required in the mixture = $60.06 \times \frac{34.8430}{516.534}$ gm.
 = 4.0516 gm.

Corrected ratio of coke = $\frac{100}{60.9} \times 24.02$ = 39.442

\therefore Amount of coke required in the mixture = $39.442 \times \frac{34.8430}{516.534}$ gm.
 = 2.6608 gm.

Amount of ash in coke = 30.2%

" " Fe_2O_3 " " = 25.904%

\therefore " " " " 1 gm coke = $\frac{30.2}{100} \times 1 \times \frac{25.904}{100}$ gm.
 = 0.07823 gm.

Calculated ratio of Fe_2O_3 to be added = 7.1874

Corrected " " " " " " = $7.1874(39.442 \times 0.07823)$ gm.
 = 4.1019 gm

\therefore Amount of Fe_2O_3 required in the mixture = $4.1019 \times \frac{34.8430}{516.534}$ gm.
 = 0.2767 gm.

Wt. of CaSO_4 in 1 gm pellet = $\frac{408.438}{516.534 + 60.06 + 39.442 + 4.1019} \times 1$
 = 0.6586 gm.

Wt. of coke in 1 gm pellet = $\frac{39.442 \times 1}{620.1379}$ = 0.0636 gm. gm.

Wt. of S in 1 gm pellet = $0.0636 \times \frac{5.3}{100}$ = 0.004007 gm

\therefore CaSO_4 equivalent to the above Wt. of

S contained in coke in 1 gm pellet = $0.004007 \times \frac{136.146}{32.06}$ gm.
 = 0.017 gm

Table 8.1.29.

System XII.

3 Gypsum : 1 SiO_2 : 2 Coke : 0.004501 Fe_2O_3
 1400°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc 0.1 N NaOH used	Sulphide titration	
			cc N/20 KBrO_3 used	cc N/100 KBrO_3 used
Wt. of boat = 6.0425	1	57.0	25.4	
do. + pellet= 7.0392				
Wt. of boat = 5.8876	1	54.1	19.0	
do. + pellet= 6.8210				
Wt. of boat = 5.8503	5	80.75		nil
do. + pellet= 6.8160				
Wt. of boat = 6.0906	5	80.45		nil
do. + pellet= 7.0600				
Wt. of boat = 5.9696	10	76.3		nil
do. + pellet= 6.8754				
Wt. of boat = 5.7853	10	74.4		nil
do. + pellet= 6.6541				
Wt. of boat = 5.8696	20	78.8		nil
do. + pellet= 6.7619				
Wt. of boat = 5.8872	20	82.0		nil
do. + pellet= 6.8269				

Observations:--

Exfoliation was followed by sintering. The colour was from light brown to dark chocolate with the rise in the time of heating.

Table 8.1.30.

System XII.

3 Gypsum : 1 SiO_2 : 2 Coke : 0.04501 Fe_2O_3 .
 1400°C.

Wt. of CaSO_4 in 1 gm pellet = 0.6586 gm.

CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.017 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	0.9967	0.6564	0.3881	0.0169	0.3712	56.551	0.04582	6.980
1	0.9334	0.6147	0.3683	0.0159	0.3524	57.329	0.03427	5.575
5	0.9657	0.6360	0.5498	0.0164	0.5334	83.868	nil	nil
5	0.9694	0.6384	0.5477	0.0165	0.5312	83.208	nil	nil
10	0.9058	0.5956	0.5195	0.0154	0.5041	84.637	nil	nil
10	0.8688	0.5722	0.5065	0.0148	0.4917	85.931	nil	nil
20	0.8923	0.5877	0.5365	0.0152	0.5213	88.702	nil	nil
20	0.9397	0.6189	0.5583	0.0160	0.5423	87.623	nil	nil

SYSTEM XII.

3 Gypsum : 1 Silica : 2 Coke : 0.04501 Fe_2O_3

1400°C.

(Oxidising Atmosphere)

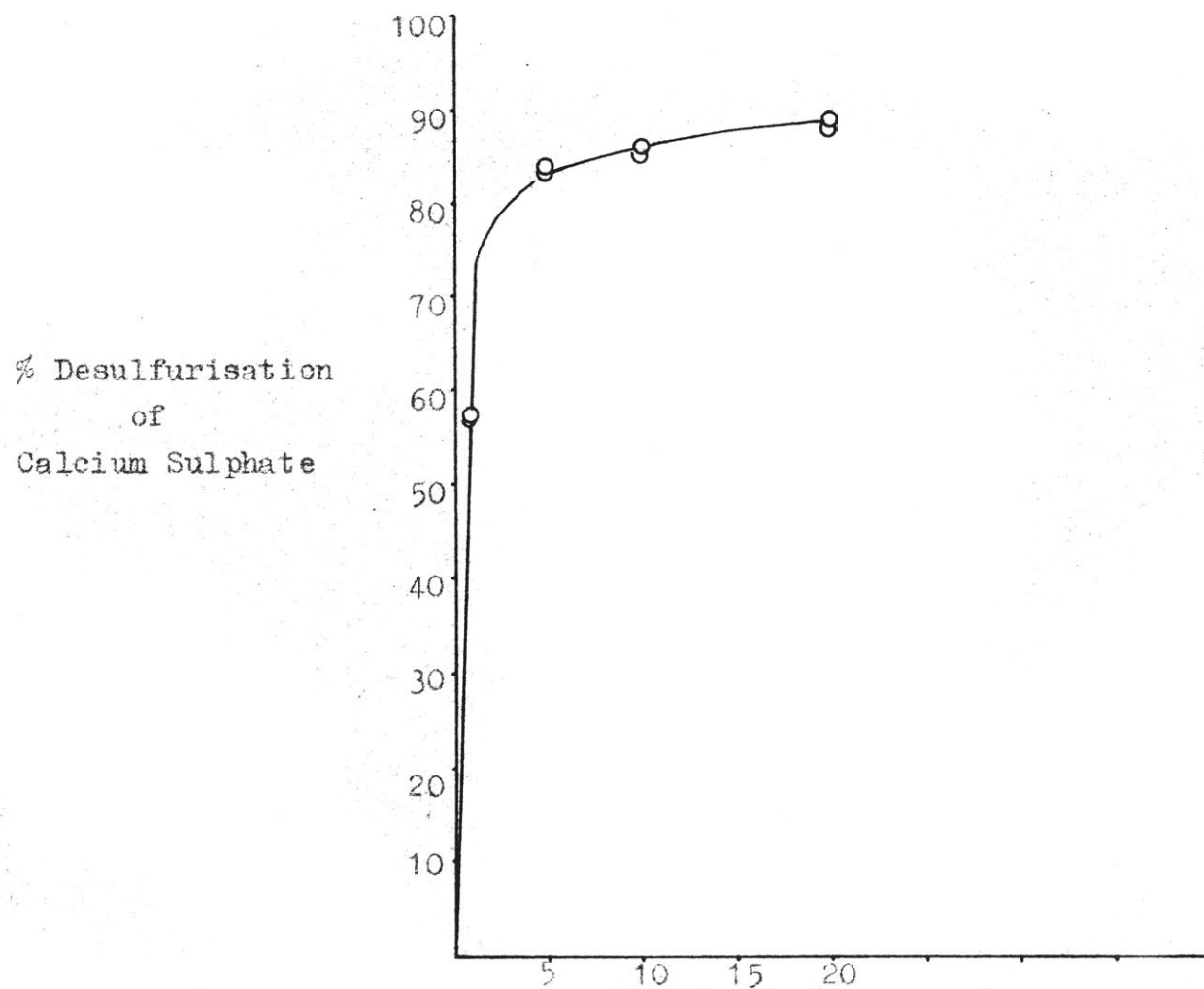
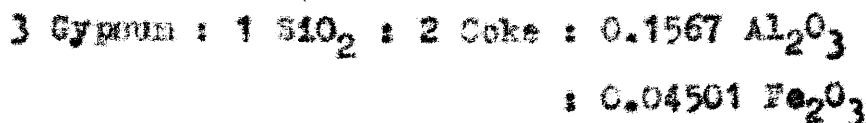


Fig. 8.1.9

System XIII.



Weight of gypsum taken = 43.6811 gm.

$$\text{Amount of SiO}_2 \text{ required in the mixture} = 60.06 \times \frac{43.6811 \text{ gm}}{516.534} \\ = 5.0793 \text{ gm}$$

$$\text{Corrected ratio of coke} = \frac{100}{60.9} \times 24.02 = 39.442 \text{ gm}$$

$$\therefore \text{Amount of coke required in the mixture} = 39.442 \times \frac{43.6811 \text{ gm}}{516.534}$$

$$= 3.3356 \text{ gm.}$$

$$\text{Amount of Fe}_2\text{O}_3 \text{ required in the mixture} = 4.1019 \times \frac{43.6811}{516.534}$$

$$= 0.3469 \text{ gm.}$$

$$\text{Amount of Al}_2\text{O}_3 \text{ required in the mixture} = 12.4759 \times 0.00457 \\ = 1.0550 \text{ gm.}$$

Weight of CaSO_4 in 1 gm pellet =

$$\frac{408.433}{516.534 + 39.442 + 12.4759 + 4.1019}$$

$$\times 1 \text{ gm.}$$

$$= 0.6456 \text{ gm.}$$

$$\text{Wt. of coke in 1 gm pellet} = \frac{39.442}{632.6138} \times 1 = 0.06235 \text{ gm}$$

$$\text{Wt. of S in 1 gm pellet} = 0.06235 \times \frac{6.3}{100} = 0.003928 \text{ gm}$$

*. CaSO_4 equivalent to ^{the} wt. of S

$$\text{contained in coke in 1 gm pellet} = 0.003928 \times \frac{136.146}{32.06}$$

$$= 0.01668 \text{ gm}$$

Table 8.1.31. (cont'd)

Weights (gm)	Time	H_2SO_4 tit- ration cc 0.1 N NaOH used	Sulphide titration	
			cc N/20 K_2CrO_7 used	cc N/100 K_2CrO_7 used
Wt. of boat = 6.2001 do. + pellets = 7.1930	1 hr	86.1		nil
Wt. of boat = 5.8810 do. + pellet = 6.8680	1 "	86.3		nil
Wt. of boat = 5.8449 do. + pellet = 6.7845	2 "	89.0		nil
Wt. of boat = 5.7768 do. + pellet = 6.7457	2 "	91.4		nil
Wt. of boat = 5.9642 do. + pellet = 6.9610	3 "	95.1		nil
Wt. of boat = 6.0379 do. + pellet = 6.9607	3 "	89.2		nil

Observations:

Effelation occurred after heating for one minute.
Slate brown color was obtained after heating for 5
minutes and above.

Table 8.1.32.

System XIII.

3 Gypsum : 1 Silica : 2 Coke : 0.1567 Al_2O_3 : 0.04501 Fe_2O_3 .
1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.6456 gm.

CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.01668 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	0.9319	0.6016	0.3581	0.0155	0.3426	56.948	0.03932	6.536
1	0.9137	0.5899	0.3649	0.0152	0.3497	59.281	0.03058	5.184
5	0.9348	0.6035	0.5277	0.0156	0.5121	84.855	nil	nil
5	0.9375	0.6053	0.5277	0.0156	0.5121	84.603	nil	nil
10	0.9054	0.5845	0.5199	0.0151	0.5040	86.228	nil	nil
10	0.9374	0.6050	0.5341	0.0156	0.5185	85.702	nil	nil
20	0.9299	0.6003	0.5355	0.0155	0.5200	86.623	nil	nil
20	0.9776	0.6311	0.5682	0.0163	0.5519	87.450	nil	nil
30	0.9456	0.6105	0.5535	0.0158	0.5377	88.075	nil	nil
30	0.9604	0.6200	0.5624	0.0160	0.5464	88.129	nil	nil

Table 8.1.32 (cont'd).

Time (hrs)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm) Total CaSO_4 equiv-Correct- (a) alent to the ed wt. of S in (a-b) coke (b)	% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
1	0.9929	0.6410	0.5862 0.0166	0.5696	88.861	nil nil
1	0.9870	0.6372	0.5876 0.0165	0.5711	89.626	nil nil
2	0.9396	0.6066	0.5991 0.0157	0.5834	96.175	nil nil
2	0.9689	0.6255	0.6223 0.0162	0.6061	96.898	nil nil
3	0.9968	0.6435	0.6543 0.0166	0.6377	99.099	nil nil
3	0.9228	0.5958	0.6073 0.0154	0.5919	99.345	nil nil

SYSTEM XIII.

3 Gypsum : 1 Silica : 2 Coke : $0.1567 \text{ Al}_2\text{O}_3$: $0.04501 \text{ Fe}_2\text{O}_3$
 1400°C

(Oxidising Atmosphere)

Points showing active desulphurisation by Carbon are marked

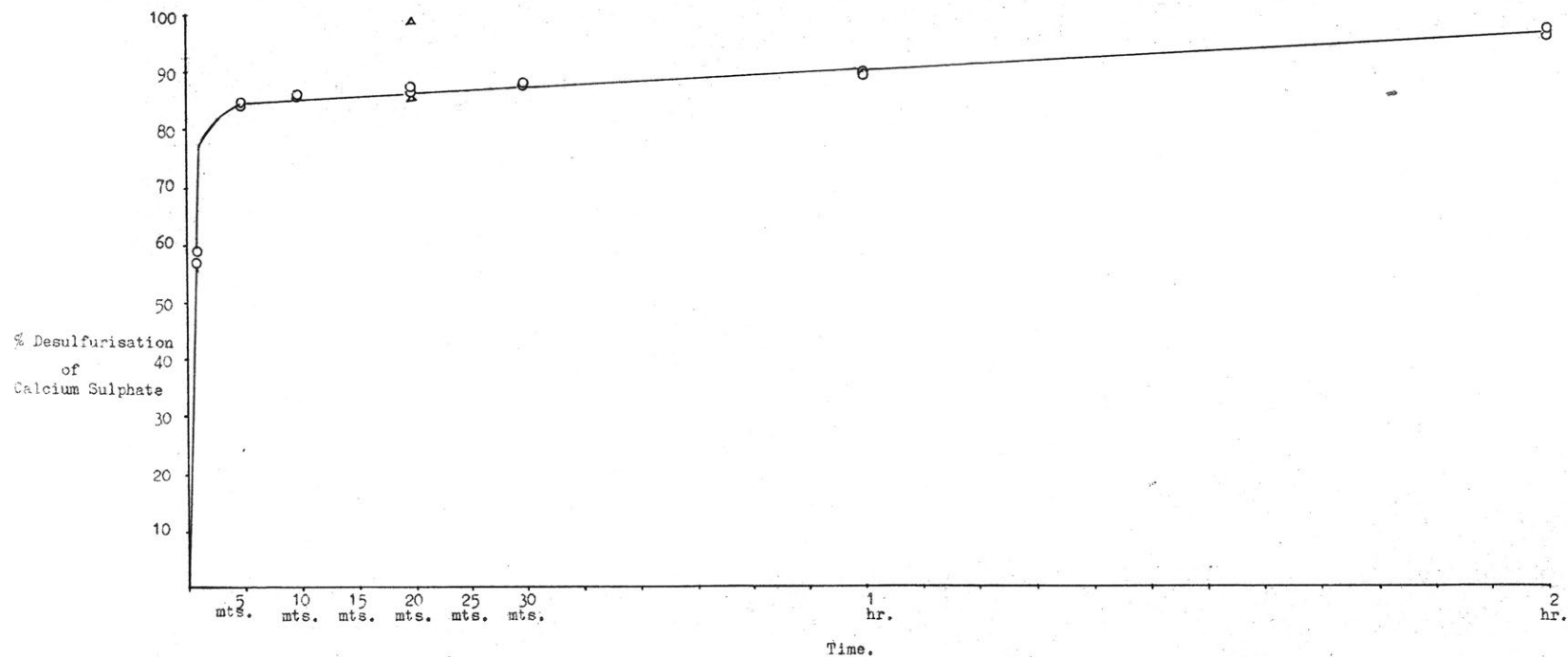


Fig. 8.1.10

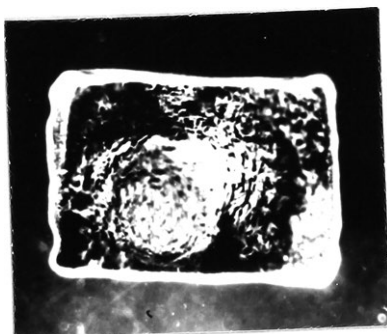


Fig. 8.1.11
Exfoliation of the pellet in
System XIII, after heating for
one minute at 1400°C .



Fig. 8.1.12
The same pellet after heating for
20 minutes at 1400°C .

II. Study of the Cement Clinker.

The Quenching Method:-

The quenching method was used to determine the equilibrium relationships between different phases in silicate and other systems involving a high melting point. It could also be used in many cases to elucidate phase relationships in other systems where, for reasons such as extensive super cooling other method may fail.

The work was divided into 3 successive operations:-

- (1) Preparation of the cement mixtures.
- (2) Heating and quenching of the charge.
- (3) Microscopic examination of the quenched charge.

(1) Preparation of the Cement Mixtures:-

The ratios of the constituents of System XIII were so selected as to give a good general-purpose cement, of a high tricalcium silicate content. Theoretically, three moles of lime supplied by 3 moles of calcium sulphate should combine with one mole of silica at high temperatures to give tricalcium silicate. The percent ratio of $3\text{CaO} : 1 \text{ silica}$ is equal to 73.6 : 26.4, on the weight basis. The phase diagram of the system $\text{CaO} - \text{SiO}_2$ by Rankin and Wright (Fig. 8-2/3) shows the formation of tricalcium silicate with this composition

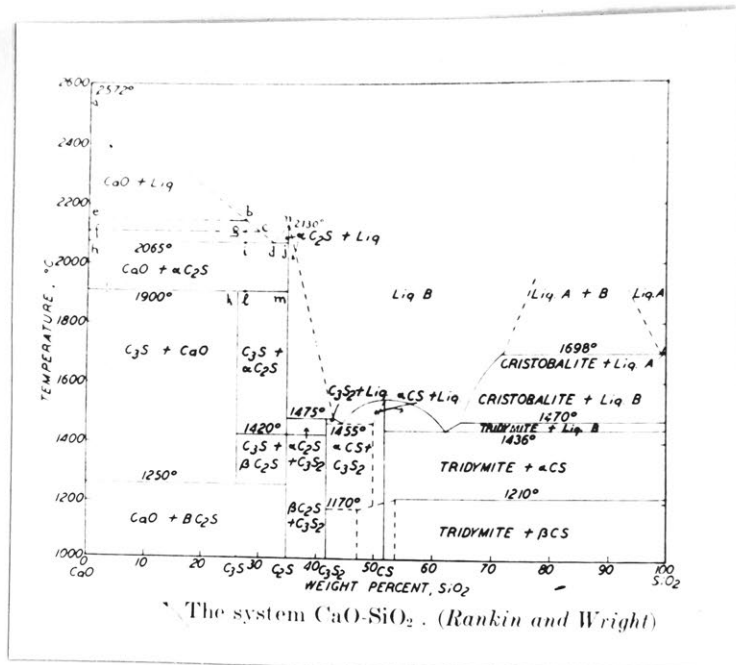


Fig. 8.2.13

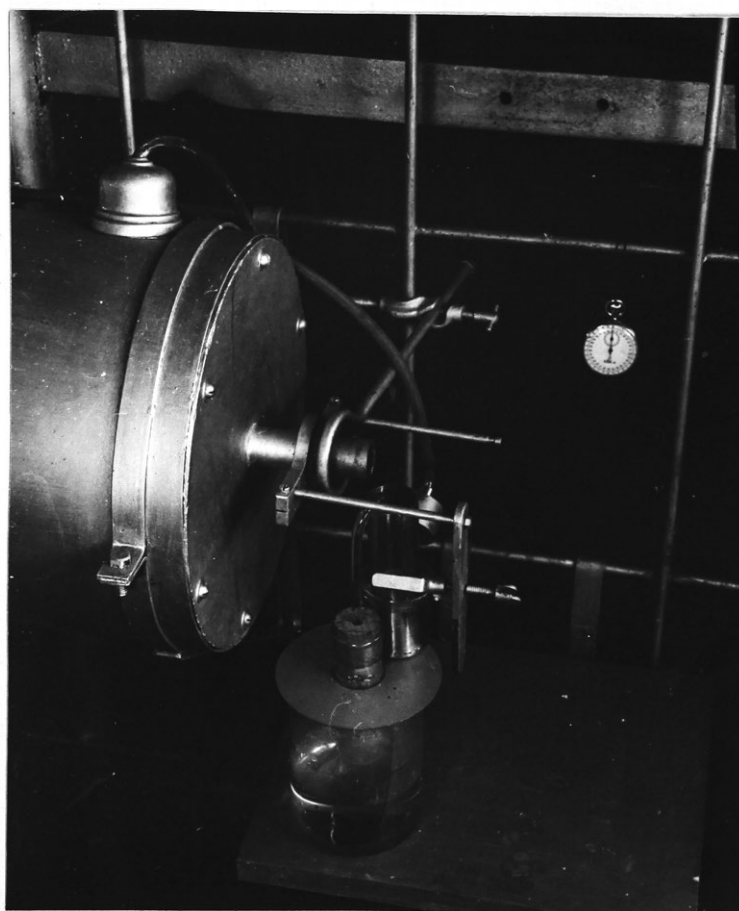


Fig. 8.2.14

Arrangement of equipment for
quenching the cement clinker.

at 1400°C . Excess of gypsum was avoided to eliminate the melts in the kiln.

The pellets of the composition 3 gypsum : 1 silica : 2 coke : $0.04501 \text{ Fe}_2\text{O}_3$: $0.1567 \text{ Al}_2\text{O}_3$ were made and placed in platinum boats for heating and quenching.

(2) Heating and Quenching:-

The charge contained in the boat was heated for 3 hours at 1400°C in the reactor and then quenched with the help of liquid air to preserve the phases present at this temperature. Water was avoided as a cooling medium to eliminate the possibility of the formation of hydrates of the clinker compounds. The equipment employed for quenching has been described in Chapter V. After heating for 3 hours in the reactor the boat containing the pellet was quickly dropped into a stainless steel tube, cooled by placing in a beaker, containing liquid air. A strong jet of cold air, was simultaneously blown over the pellet. The jet was generated by placing in a beaker of water a glass tube containing liquid air, from which a delivery tube took the vapourised air to the stainless steel tube. Direct quenching in liquid air contained in a thermosflask was also successfully tried, using rubber gloves and a face mask for protection against spurling.

(3) Microscopic Examination of the Quenched Charge:-

Le Chatlier was first to appreciate that the

nature of the compounds formed during fusion and crystallization could not be revealed by chemical analysis, and that petrographic methods are the classical tools to cope with this problem. Three methods were employed for the microscopic examination of the Portland cement clinker.

(A) Refractive Index Method:-

A small amount of the liquid medium, of standard R.I and prepared by the method described in the following paragraph, was placed on a slide and a small amount of the powdered clinker was placed on it. A cover glass was then placed over the mixture. It could then be pressed readily into a thin film and determination made.

Procedure:-

Methylene iodide (R.I = 1.737) and Bromonaphthalene (R.I = 1.658) were used to prepare solutions of different refractive indices to match the R.I's of the different components of cement. Homographic chart was prepared to get the required ratios in which the components were added to get the required refractive index. The components were added from a microburette and the number of drops of each component delivered per cc were also noted to facilitate the addition of the fractions of the liquid volumes. The R.I's were finally adjusted by means of a Leitz microrefractometer. To prepare solutions of R.I's less than 1.658 α -chloronaphthalene was employed to lower them to the required value.

Methylene iodide was preserved with granulated tin, otherwise it became dark. To save the solutions from the effect of light, they were kept in 10 cc corked tubes, painted black on outside and placed in a slotted wooden stand. The estimations were done with the help of a Leitz M.O.P. microscope.

The study of the remaining properties of the clinker compounds was done by the following methods:-

- (B) Examination of thin sections by transmitted light.
- (C) Examination of polished and suitably etched sections by reflected light.

The thin and polished sections were prepared by the Geology Department, University of Technology, as follows:-

(a) Preparation of Thin Sections:-

The slice of the clinker was smoothed down on one side using carborundum of the following grades in order, on a glass slab:-

- (i) 220
- (ii) 400 (also called 3F)
- (iii) 600

The slice was then mounted on a glass slide by means of Canada balsam, and then ground on rotating wheel, using 220 carborundum. Fine polishing was then done by 3F and 600 carborundum. At this stage the specimen was constantly checked under the microscope. Some Canada balsam was molten on a cover glass by placing it on a hotplate and after heating the balsam on the specimen slide in the same way, the cover glass was fixed in place and the slide cleaned and cooled. The thickness was of the order of 0.04 inches. Under polarised light, any quartz or feldspar embedded in a slide of suitable thickness is revealed by grayish or creamy colour.

(b) Preparation of Polished Sections:-

The process consisted of two main parts:-

- (i) rough polishing
- (ii) fine polishing.

(i) Rough Polishing:-

The clinker specimens were cut and ground by hand with 400 grade carborundum. "Plastrene 47" plastic compound was then prepared for embedding the specimens by mixing the following components in the given order to avoid explosion:-

PolyLite 8000

100 volumes

Catalyst No. 2	1.5 volumes
Promoter No. 2	1 unit volumes

These were supplied by Reichhold Chemicals Inc. Pty. Ltd., Rosebery. A little Plastrene 47 was poured in small glass forms (prepared by cutting off more than half of 30 mm beakers and the specimen was placed in it with face downward and then the rest of the form was filled up to 15 - 17 mm height). The plastic took up to 12 hours to set, after which it was tapped out and ground roughly on both sides with 400 grade carborundum. The specimen was then ground with 600 carborundum and then with ultrafine emery grade 304.

(ii) Fine Polishing:-

Fine polishing was done on 4 laps. The first one used was a stationary wax lap, with a top of "1904 - Microcrystalline Wax" (supplied by Vacuum Oil Co.) impregnated with ultrafine Emery Grade 304. Polishing on this wax lap was done on the plateaux of the wax-surface. The second one was a cloth topped lap impregnated with diamond dust grade 4u - 8u. The dust was in a paste-like base. The third one was a rotating cloth topped lap impregnated with 0u - 1u grade diamond dust and the polishing process was finished off on a stationary cloth-lap, also with 0u - 1u diamond dust.

In the preparation of thin and polished

sections kerosene oil was used instead of water.

(C) Etching of the Polished Sections:-

The polished sections were etched by the following reagents in the given order:-

- (i) Distilled water 2 seconds
- (ii) 1% HNO_3 solution in 5 seconds
ethyl alcohol
- (iii) 10% KOH.aq.solution 15 seconds

Distilled water served to differentiate CaO . MgO and crystalline dark interstitial material. HNO_3 solution differentiated between C_3S , C_2S , C_4AF and total dark interstitial material, and is useful when clinker is low in Fe_2O_3 such as may occur when C_4AF has crystallised from the liquid, while KOH is satisfactory for all glasses irrespective of their iron content. The use of KOH turned the interstitial material dark, revealing the crystals of C_4AF , which otherwise remain unobserved against a white background.

(d) Identification of the Clinker Components:-

On microscopic examination with the petrological microscope, the following constituents were identified, by the properties given below. In the case of inter-

ference figure and birefringence only transmitted light was used. The work was done with the assistance of Dr. L. J. Lawrence of the Geology Department, University of Technology.

(1) Tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$):-

Refractive indices:-

$$\omega = 1.722$$

$$\varepsilon = 1.716$$

Uniaxial negative.

Relief:-

High. The average refractive index is 1.718.

Birefringence:-

Weak; polarising in 1st order greys.

Form:-

Granular, there were also large equant crystals, circular or lath shaped.

Cleavage:-

Irregular partings.

Colour:-

Stained yellowish orange.

Distinguishing features:-

The almost uniaxial figure, the high refractive index and low birefringence are all distinctive.

(2) Brownmillerite. or tetracalcium aluminoferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$):-

Refractive indices:-

α = 1.96

β = 2.01

γ = 2.04

orthorhombic.

Relief:-

Very high.

Birefringence:-

Crystals were anisotropic but the polarisation colour was masked by the natural colour.

Form:-

Equant with imperfect cleavage.

Colour:-

Marked pleochroism from yellow to brown, was more transparent than mono or dicalcium ferrite.

Distinguishing features:-

Biaxial character, colour and pleochroism.

(e) Phase composition:-

In the four specimens, there were two crystalline phases present in addition to glass, the phase composition

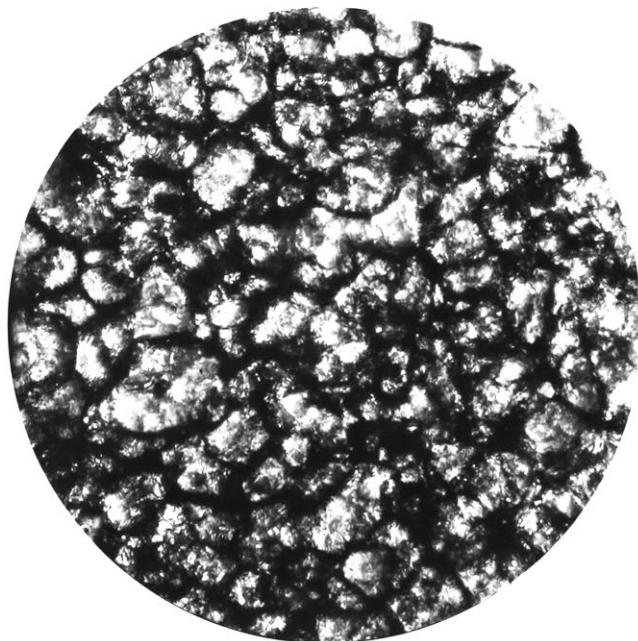


Fig. 6.2.15
Liquid air quenched clinker.
Transmitted light. X 194.

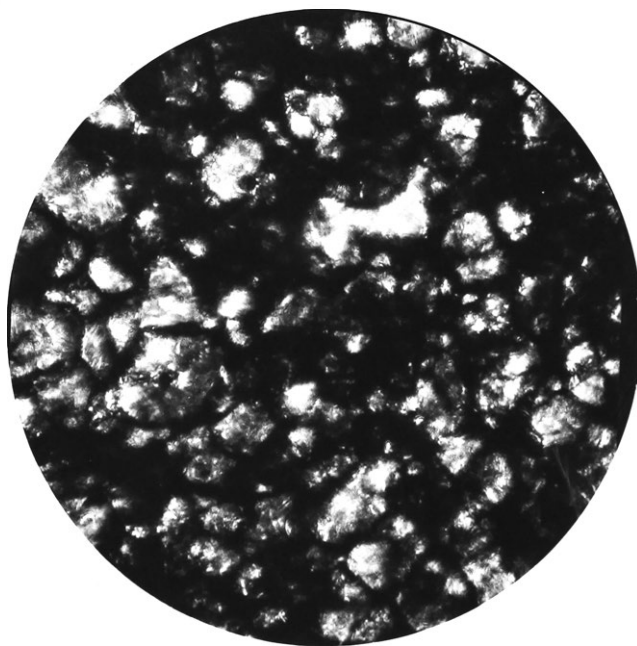


Fig. 8.2.16
Liquid air Quenched clinker.
Transmitted light.
crossed nicols. x 194.

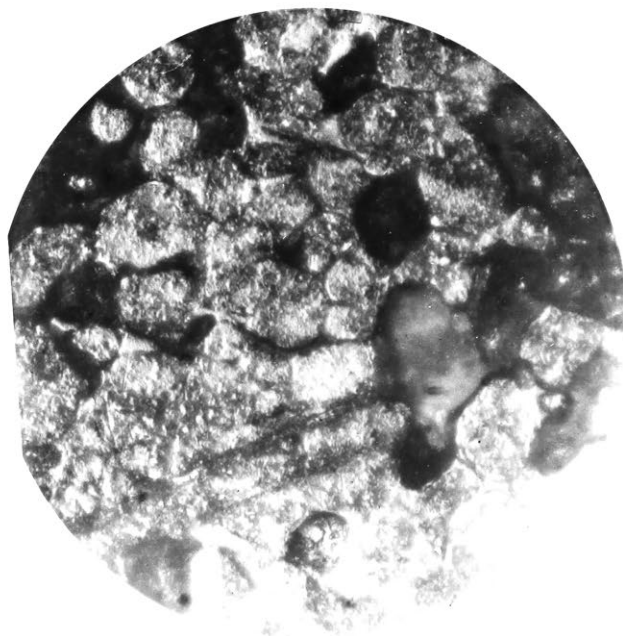


Fig. 8.2.17

Liquid air quenched clinker.
Polished section finally etched
with aq. KOH solution. Reflected
light. $\times 194$.

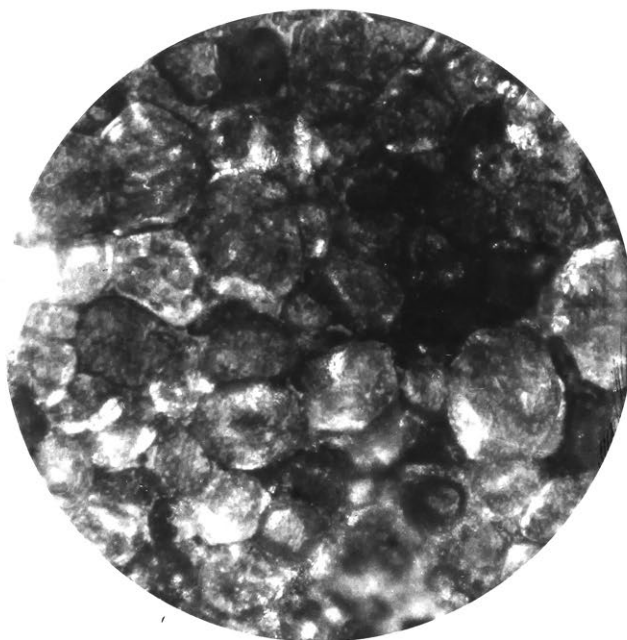


Fig. 8.2.18

Liquid air quenched clinker. Polished section, finally etched with eq. KOH solution. Reflected light. Crossed nicols. X 194.



Fig. 8.2.19

Liquid air quenched clinker. Another view of the polished section, finally etched with aq. KOH solution. Reflected light. X 194.

of the clinker was as follows:-

- | | | |
|----|---------------------|--------|
| 1. | Tricalcium silicate | 90% |
| 2. | Brownmillerite | 6 - 8% |
| 3. | Glass | 2 - 4% |

(f) Photography of the thin and polished sections with
Vickers Microscope:-

Vickers microscope was used for photographing the thin and polished sections. As the crystals obtained were large, the magnification used was 194 instead of 500. Photographs were taken, using transmitted light in the case of thin sections and reflected light in the case of polished sections, with and without crossed nicols.

III. STUDY OF REACTION MECHANISMS.

A. Oxidising Atmospheres:-

System XIV.

Gypsum (Two sets of the pellets
of different size).

$$\text{Weight of CaSO}_4 \text{ in 1 gm pellet} = \frac{136.146}{172.178} = 0.791 \text{ gm}$$

Table 8.3.33

System XIV.

Gypsum (Two sets, of the pellets of
different size).

1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ titration cc 0.1N NaOH used
Wt. of boat = 5.8579	1	0.35
do. + pellet= 6.3552		
Wt. of boat = 6.0202	1	0.35
do. + pellet= 6.9763		
Wt. of boat = 5.8412	5	2.6
do. + pellet= 6.3426		
Wt. of boat = 6.0747	5	2.4
do. + pellet= 7.0514		
Wt. of boat = 6.0220	10	5.65
do. + pellet= 6.5136		
Wt. of boat = 6.1642	10	5.7
do. + pellet= 7.1520		

Table 8.3.33 (cont'd)

Weights (gm)	Time (mts)	H ₂ SO ₄ titration cc 0.1N NaOH used
Wt. of boat = 5.9533	20	9.5
do. + pellet = 6.4629		
Wt. of boat = 6.0710	20	10.15
do. + pellet = 7.0580		

Observations:-

The effect of heating on pellets was more pronounced at the bottom, although no melts were obtained up to 5 minutes. From 5 minutes upwards the contents of the boats fused with the formation of excess of CaO.

Table 8.3.34.

System XIV.

Pure Gypsum.

$$\text{Weight of CaSO}_4^{1400^\circ\text{C}} \text{ in 1 gm pellet} = 0.791 \text{ gm.}$$

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)	% Desulfurised CaSO_4
1	0.4973	0.3934	0.002383	0.606
1	0.9551	0.7563	0.002383	0.315
5	0.5014	0.3966	0.01770	4.463
5	0.9767	0.7726	0.01634	2.115
10	0.4916	0.3889	0.03847	9.892
10	0.9878	0.7813	0.03881	4.967
20	0.5096	0.4031	0.06468	16.046
20	0.9870	0.7807	0.06911	8.852

SYSTEM XIV.

Gypsum

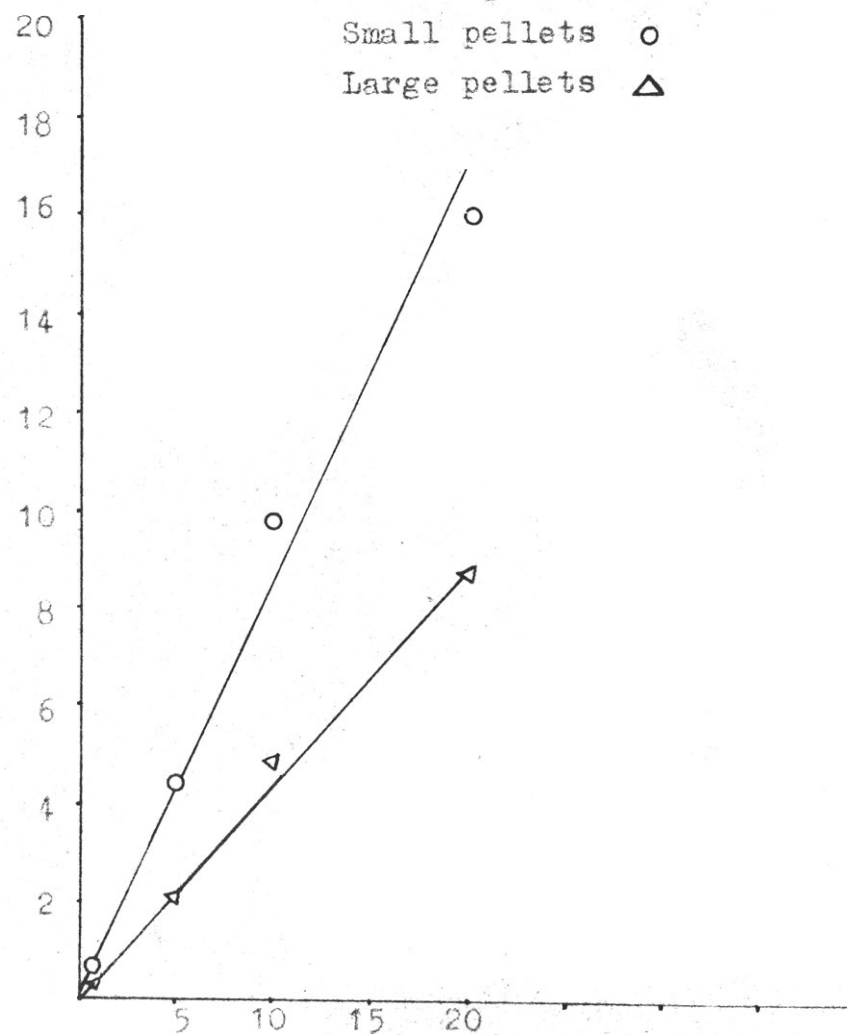
1400°C.

(Oxidising Atmosphere)

Small pellets ○

Large pellets △

% Desulfurisation
of
Calcium Sulphate



Time (mts).

Fig. 8.3.20

System XV.
Calcium Sulphide.

Analysis of B.P.C. CaS (May & Baker):-

H_2S evolved from 2 samples of CaS was absorbed in Ammoniacal zinc sulphate solution and titrated against N/10 $KBrO_3$ solution, after acidification in the usual way:-

$$\begin{aligned} \text{(i) Weight of sample (1)} &= 0.0899 \text{ gm} \\ \text{N/10 } KBrO_3 \text{ used} &= 11.25 \text{ cc} \\ \therefore \% \text{ CaS} &= \frac{11.25 \times 0.003607705}{0.0899} \times 100 \\ &= 45.15 \end{aligned}$$

$$\begin{aligned} \text{(ii) Weight of sample (2)} &= 0.1020 \text{ gm} \\ \text{N/10 } KBrO_3 \text{ used} &= 12.85 \text{ cc} \\ \therefore \% \text{ CaS} &= \frac{12.85 \times 0.003607705}{0.1020} \times 100 \\ &= 45.45 \end{aligned}$$

$$\therefore \% \text{ CaS in the B.P.C. Quality sample (mean)} = 45.3$$

CaSO₄ Content of B.P.C. CaS :-

Procedure:-

Two samples of CaS were weighed. The sulphide was decomposed with HCl in silica dishes. The sulphate content remained undissolved. The samples were

dried, heated with Na_2CO_3 , and then boiled after adding 50 cc of water. The contents were transferred to a beaker, and neutralised with HCl. 50 cc of 1 : 5 HCl were then added and boiling continued for 5 minutes. The solution was filtered and boiled. While boiling 20 cc of a boiling 10% solution of BaCl_2 were added. After digesting the precipitate for an hour, it was filtered, washed, dried and ignited at bright red heat. A drop of H_2SO_4 was used to oxidise any sulphide formed by the reduction of SO_4 .

Calculations:-

$$(i) \text{ Weight of sample (1) } = 1.0356 \text{ gm}$$

$$\text{Weight of crucible } = 12.9397 \text{ gm}$$

$$\text{do.} + \text{BaSO}_4 \text{ ppt} + \text{ash} = 13.6028 \text{ gm}$$

$$\text{Weight of Whatman 540 paper ash} = 0.00007 \text{ gm}$$

$$\therefore \text{ weight of BaSO}_4 \text{ ppt.} = 0.66303 \text{ gm}$$

$$\begin{aligned} \therefore \text{CaSO}_4 \text{ equivalent to the above weight of BaSO}_4 \\ = 0.66303 \times 0.13735 \times \frac{136.146}{32.06} \text{ gm} \end{aligned}$$

$$= 0.3867 \text{ gm.}$$

$$\begin{aligned} \therefore \% \text{CaSO}_4 \text{ in the CaS} &= \frac{0.3867 \times 100}{1.0356} \\ &= 37.341 \end{aligned}$$

- (11) Weight of sample (2) = 0.9944 gm
 Weight of crucible = 16.4754 gm
 do. + BaSO_4 ppt + ash = 17.1144 gm
 Weight of Whatman 540 paper ash = 0.00007 gm
 \therefore Weight of BaSO_4 ppt. = 0.63893 gm
 \therefore CaSO_4 equivalent to the above weight of BaSO_4

$$= 0.63893 \times 0.13735 \times \frac{136.146}{32.06}$$

$$= 0.3727 \text{ gm}$$

$$\therefore \% \text{CaSO}_4 \text{ in the CaS} = \frac{0.3727 \times 100}{0.9944}$$

$$= 37.48$$

$$\therefore \text{CaSO}_4 \text{ content of CaS (mean)} = 37.41\%.$$
-

Calculations of the total S in 1 gm pellet:-

$$\begin{aligned} \text{S due to CaSO}_4 &= \frac{37.411}{100} \times \frac{32.06}{136.146} \\ &= 0.0881 \text{ gm} \\ \text{S due to CaS} &= \frac{45.3}{100} \times \frac{32.06}{72.146} \\ &= 0.2013 \text{ gm} \\ \therefore \text{Total S in 1 gm pellet} &= 0.0881 + 0.2013 \\ &= 0.2894 \text{ gm} \end{aligned}$$

We know from our calculations at the very outset that,
 1cc of 0.1N NaOH = 0.00160026 gm of evolved S.

Table 8.3.35
System XV.
CaS (oxidising atmosphere)
1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ titration cc 0.1N NaOH used
Wt. of boat = 5.9607 do. + pellet= 6.8300	1	46.25
Wt. of boat = 6.1533 do. + pellet= 7.0572	5	109.6
Wt. of boat = 5.8295 do. + pellet= 6.7519	10	139.75
Wt. of boat = 6.0084 do. + pellet= 6.9673	20	145.6

Observations:-

The pellets did not fuse but became hard and compact after heating for 20 minutes. Due to the decomposition of sulphide in oxidising atmosphere a typical blistered surface was obtained.

Table 8.3.36.

System XV.

Gas (oxidising atmosphere).

Total S in 1 gm pellet $\stackrel{1400^{\circ}\text{C}}{=} 0.2894$ gm.

Time (mts)	Weight of pellet (gm)	Weight of total S in pellet (gm)	Weight of evolved S (gm)	% Desulfurisation
1	0.8693	0.2516	0.07401	29.415
5	0.9039	0.2616	0.1754	67.049
10	0.9224	0.2669	0.2236	83.777
20	0.9589	0.2775	0.2330	83.964

SYSTEM XV.
CaS (B. P. C.).
1400°C

(Oxidising Atmosphere).

% Total
Desulfurisation.

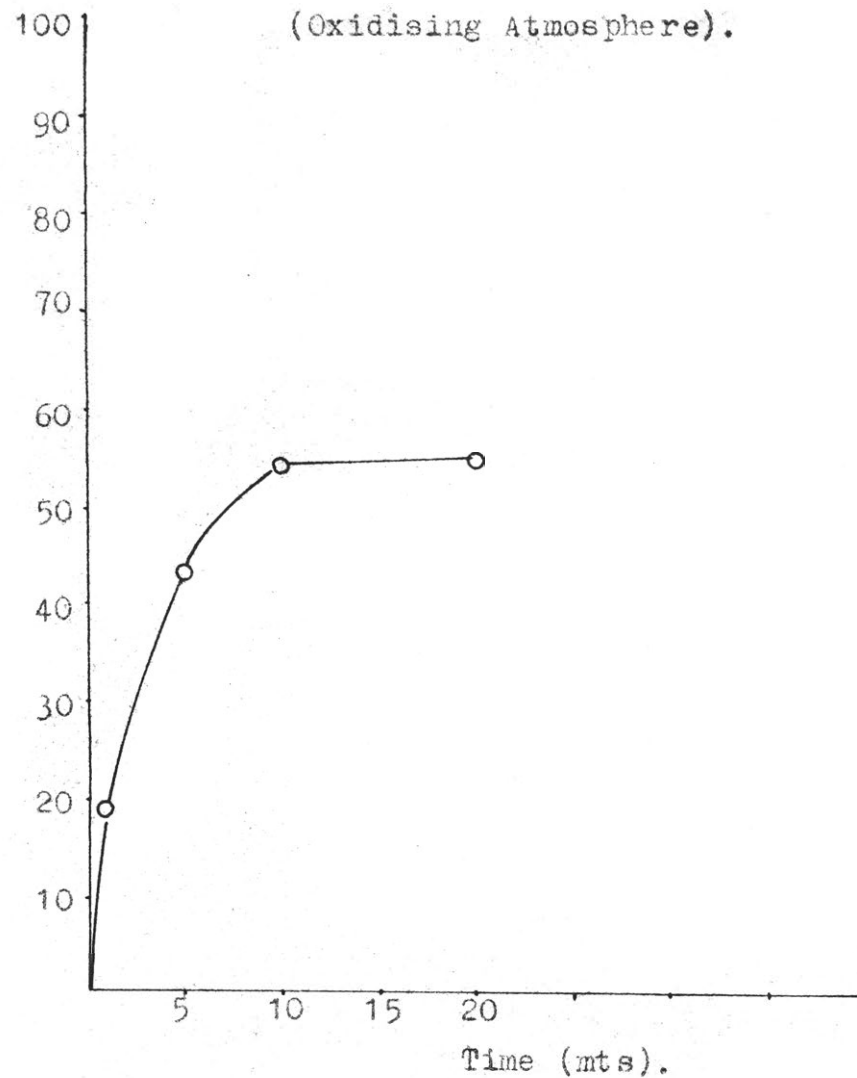


Fig. 8.3.21

Analysis of the pellet for sulphate content, after heating for 20 minutes:-

Procedure:-

The pellet after heating for 20 minutes, was powdered and the sulphate content extracted after heating with sodium carbonate in the usual way. The sulphate was precipitated as BaSO_4 , as already explained.

Calculations:-

Original weight of pellet before heating = 0.9589 gm

Weight of crucible = 16.4798 gm

do. + BaSO_4 ppt + ash = 16.7891 gm

Weight of whatman 540 filter paper ash = 0.00007 gm

\therefore weight of BaSO_4 ppt = 0.30923 gm

\therefore CaSO_4 equivalent to the above weight of BaSO_4

$$= 0.30923 \times 0.13735 \times \frac{136.146}{32.06}$$

$$= 0.1804 \text{ gm}$$

\therefore % CaSO_4 in the pellet after 20 minutes heating

$$= \frac{0.1804 \times 100}{0.9589} = 18.813$$

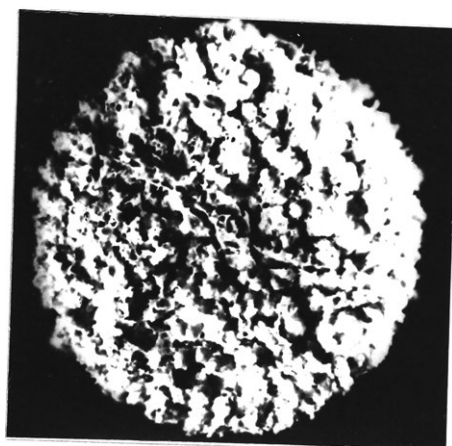


Fig. 8.3.22
Appearance of CaS pellet after heating
for 20 minutes at 1400°C .

Calcium sulphide left in the pellet after 20 minutes heating:-

Original wt. of the pellet = 0.9589 gm

Weight of CaS present in it = $0.9589 \times \frac{45.3}{100}$

= 0.4344 gm

Wt. of sulphur evolved after heating for 20 minutes
= 0.2330 gm

Wt. of sulphate sulphur in the pellet after heating
for 20 minutes = 0.30923×0.13735 gm
= 0.04247 gm

∴ Wt. of evolved sulphur + sulphate sulphur
= 0.2755 gm

Wt. of total sulphur originally present = 0.2775 gm

∴ Wt. of sulphide sulphur left in pellet = 0.002 gm

∴ Wt. of undecomposed CaS in the pellet

= $0.002 \times \frac{32.06}{72.146}$ gm

= 0.0008888 gm

= $0.0008888 \times \frac{100}{0.4344}$ gm

= 0.2%

B. Nitrogen Atmospheres:-

All the systems to follow were studied in nitrogen atmospheres. The evolved gases contained only SO_2 . No H_2S , CO and CS_2 were obtained. A railroad type sulphur condenser was connected in between the reactor and SO_2 absorber. The condenser was surrounded by ice and HCl mixture. In order to be sure that no sulphur condensed in the cooler portions of the furnace or in the outlet tube, the length of the reactor tube on the outlet side, was shortened by $4\frac{1}{2}$ inches and the flow of cooling air stopped to keep the end hot. In addition the outlet tube was wound with resistance wire and heated to just under its softening point. No weighable sulphur evolved.

System XVI.

Nitrogen Atmospheres.

3 Gypsum (anhydrous) : 2 Coke.

Anhydrous gypsum was prepared by heating to constant weight at $215^\circ - 230^\circ\text{C}$.

Weight of anhydrous gypsum taken = 21.0918 gm

Corrected ratio of coke = $\frac{100}{60.9} \times 24.02$

60.9

= 39.442 gm

∴ Amount of coke required in the mixture

= $\frac{39.442 \times 21.0918}{408.438}$ gm

408.438

= 2.0368 gm

$$\begin{aligned}\text{Weight of CaSO}_4 \text{ in 1 gm pellet} &= \frac{408.438}{447.88} \times 1 \\ &= 0.9119 \text{ gm}\end{aligned}$$

$$\begin{aligned}\text{Weight of coke in 1 gm pellet} &= \frac{39.442}{447.88} \times 1 \\ &= 0.08806 \text{ gm}\end{aligned}$$

$$\begin{aligned}\therefore \text{Weight of S in 1 gm pellet} &= 0.08806 \times \frac{6.3}{100} \text{ gm} \\ &= 0.005548 \text{ gm}\end{aligned}$$

$$\begin{aligned}\therefore \text{CaSO}_4 \text{ equivalent to weight of S contained in coke} \\ \text{in 1 gm pellet} &= 0.005548 \times \frac{136.146}{32.06} \text{ gm} \\ &= 0.02356 \text{ gm.}\end{aligned}$$

Table 8.3.37
 System XVI
 3 Gypsum (anhydrous): 2 Coke.
 1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1 N NaOH used	Sulphide tit- ration cc 0.1 N KBrO ₃ usdd
Wt. of boat = 6.0173 do. + pellet= 7.0125	1	100.9	16.6
Wt. of boat = 5.8381 do. + pellet= 6.7931	5	96.8	13.5
Wt. of boat = 6.1614 do. + pellet= 7.1857	10	104.0	15.2
Wt. of boat = 5.8543 do. + pellet= 6.8463	20	101.4	14.0

Observations:-

The pellets disintegrated into small fragments with muffled crackling sound, as soon as the boats were inserted in the reactor. The colour of the pellets after firing was grey and they did not stick to the boats.

Table 8.3.38.

System XVI.

3 Gypsum (anhydrous) : 2 Coke.

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.9119 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.02356 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	0.9952	0.9075	0.6869	0.0234	0.6635	73.113	0.05989	6.599
5	0.9550	0.8709	0.6591	0.0225	0.6366	73.097	0.04670	5.592
10	1.0243	0.9341	0.7081	0.0241	0.6840	73.226	0.05484	5.871
20	0.9920	0.9046	0.6904	0.0234	0.6670	73.734	0.5051	5.584

Table 8.3.39.

System XVI.

3 Gypsum (anhydrous) : 2 Coke.

1100°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit-	Sulphide tit-
		ration	ration
		cc 0.1N NaOH used	cc 0.1N KBrO ₃ used
Wt. of boat = 6.0149	1	10.00	28.6
do. + pellet = 6.9905			
Wt. of boat = 6.1621	5	66.2	28.3
do. + pellet = 7.1199			
Wt. of boat = 5.8548	10	82.7	24.85
do. + pellet = 6.7840			
Wt. of boat = 6.0180	20	86.9	23.6
do. + pellet = 6.9268			

Observations:-

No disintegration of pellets occurred at 1100°C.
The colour of the pellets after heating was greyish white
and were easy to remove from the boats.

Table 8.3.40.

System XVI.

3 Gypsum (anhydrous) : 2 Coke.

1100°C.

Weight of CaSO_4 in 1 gm pellet = 0.9119 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.02356 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurized CaSO_4 (gm)			% Desulfurized CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	0.9756	0.8896	0.0681	0.0230	0.0451	5.070	0.1032	11.601
5	0.9578	0.8734	0.4507	0.0226	0.4281	49.015	0.1021	11.689
10	0.9292	0.8473	0.5631	0.0219	0.5412	63.873	0.08965	10.581
20	0.9088	0.8287	0.5916	0.0214	0.5702	68.807	0.08514	10.274

SYSTEM XVI.

3 Gypsum (anhydrous) + 2 Coke

1400°C. ○

1100°C. △

(Nitrogen Atmosphere)

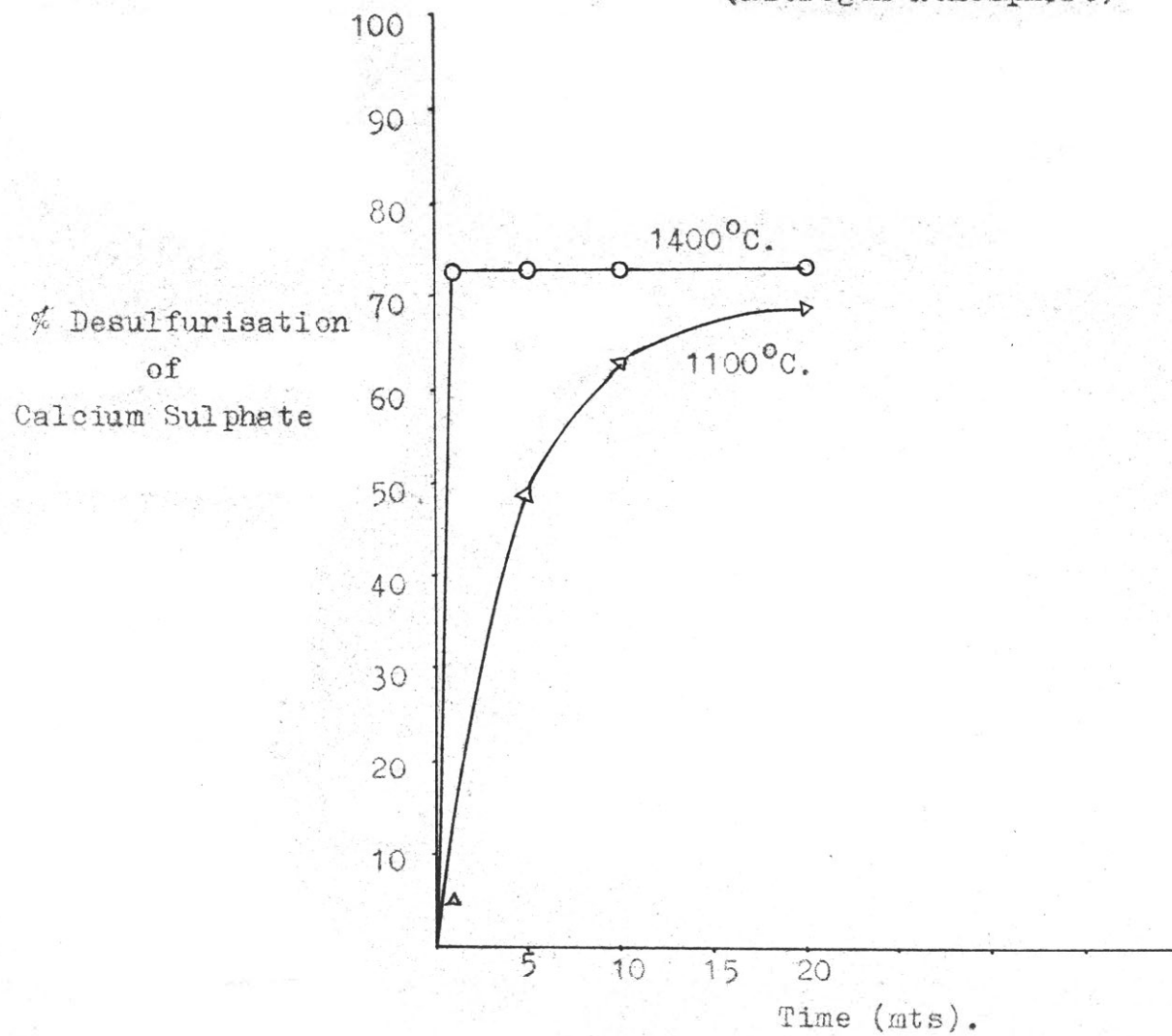


Fig. 8.3.23

Table 2.3.41.
System XVII.
3 Gypsum : 2 Coke.
1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit-	Sulphide tit-
		ration	ration
		cc 0.1N	cc 0.1N
		NaOH used	KBrO ₃ used
Wt. of boat = 6.1621	1	41.55	21.1
do. + pellet = 7.1685			
Wt. of boat = 5.8593	5	88.3	12.1
do. + pellet = 6.8762			
Wt. of boat = 6.0187	10	83.0	10.8
do. + pellet = 6.9800			
Wt. of boat = 5.8405	20	90.4	11.6
do. + pellet = 6.8794			

Observations:-

Greyish brown exfoliated pellets were obtained after heating.

Table 8.3.42.

System XVII.

3 Gypsum : 2 Coke.

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.7346 gm.

CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.01898 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	1.0064	0.7393	0.2829	0.0191	0.2638	35.682	0.07612	10.296
5	1.0209	0.7500	0.6012	0.0194	0.5818	77.573	0.04365	5.820
10	0.9613	0.7062	0.5551	0.0182	0.5469	77.442	0.03896	5.517
20	1.0389	0.7632	0.6155	0.0197	0.5958	78.066	0.04185	5.483

Table 8.3.43.
System XVII.
3 Gypsum : 2 Coke.
1100°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1 N NaOH used	Sulphide tit- ration cc 0.1 N KBrO ₃ used
Wt. of boat = 6.0150 do. + pellet = 7.0599	1	1.9	9.5
Wt. of boat = 6.1622 do. + pellet = 7.1505	5	25.75	26.4
Wt. of boat = 5.8548 do. + pellet = 6.9249	10	56.2	28.9
Wt. of boat = 6.0182 do. + pellet = 7.0004	20	78.2	17.5

Observations:--

In the 1 minute reading, the pellet decomposed on the surface only, leaving the coke and the sulphur contained in it unburnt, which was therefore not accounted for in the calculations. The pellets after firing were greyish white in colour and did not stick to the boats.

Table 8.3.44.

System XVII.

3 Gypsum : 2 Coke.

1100°C.

Weight of CaSO_4 in 1 gm pellet = 0.7346 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.01898 gm.

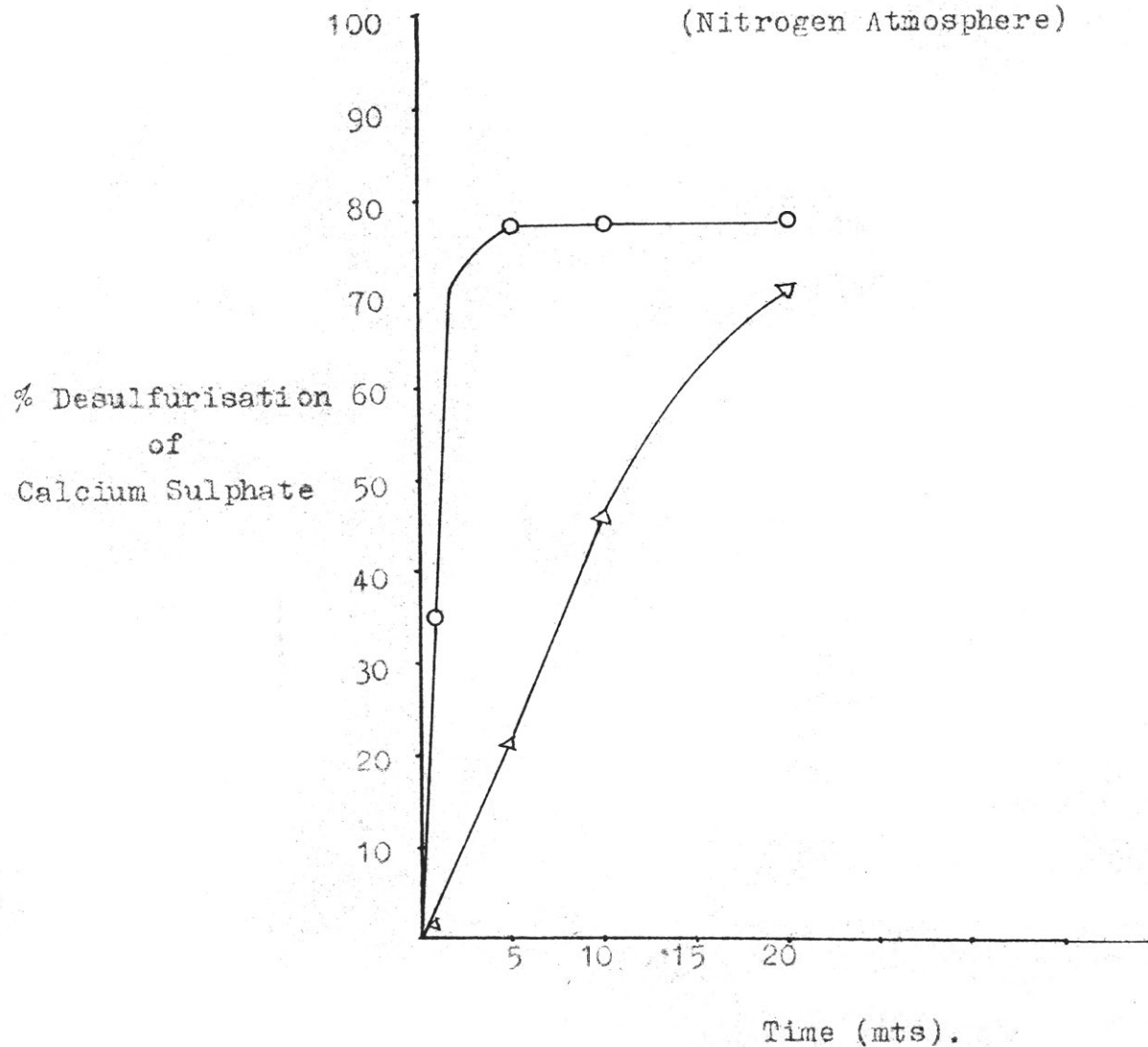
Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurized CaSO_4 (gm)			% Desulfurized CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	1.0449	0.7676	0.0129	S was un- burnt	0.0129	1.681	0.03427	4.465
5	0.9883	0.7260	0.1753	0.0188	0.1565	21.556	0.09524	13.118
10	1.0701	0.7861	0.3826	0.0203	0.3623	46.088	0.1043	13.268
20	0.9822	0.7215	0.5324	0.0186	0.5138	71.213	0.06313	8.750

SYSTEM XVII.
3 Gypsum + 2 Coke.

1400°C. ○

1100°C. △

(Nitrogen Atmosphere)



Time (mts).

Fig. 8.3.24

SYSTEM XVII.
3 Gypsum : 2 Coke
1100°C.
(Nitrogen Atmosphere)
CaS formed in the system.

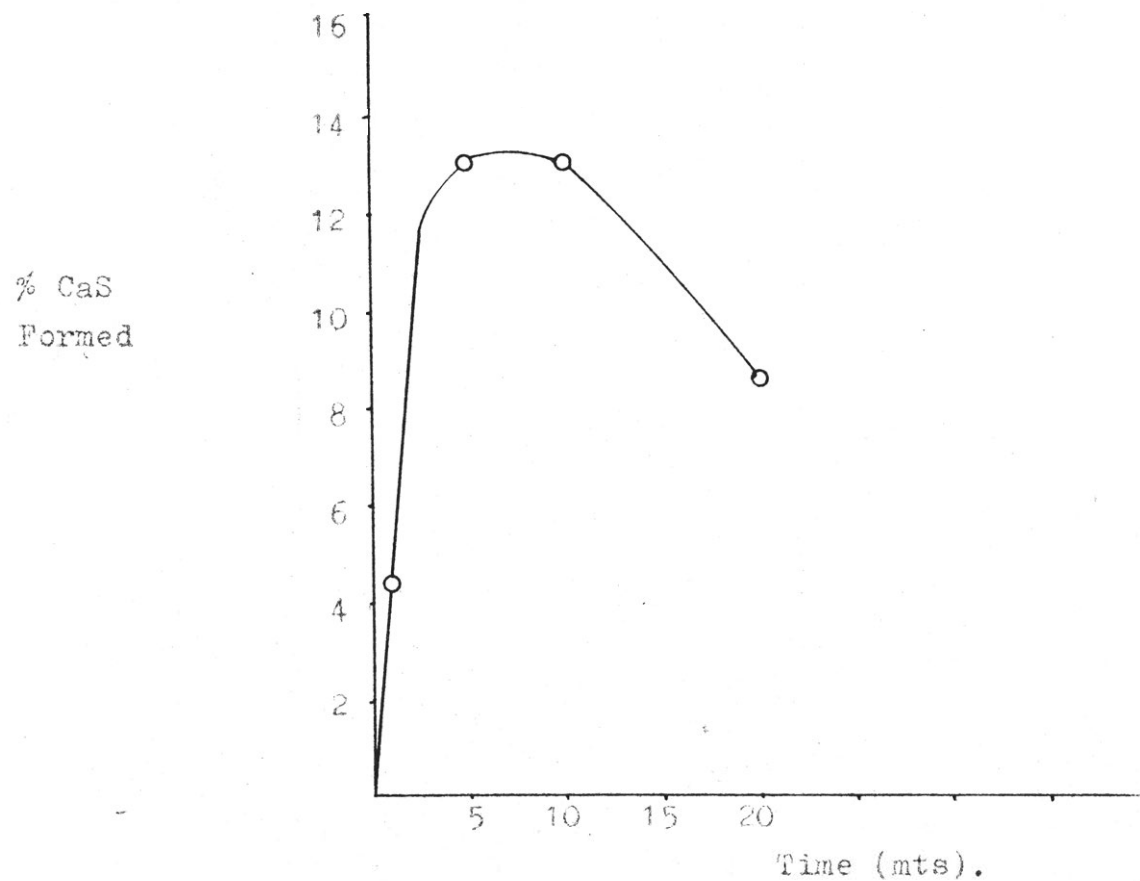


Fig. 8.3.25

System XVIII.

3 Gypsum : 2 Coke : $0.1567 \text{ Al}_2\text{O}_3$.

Weight of gypsum taken = 23.4536 gm

Corrected ratio of coke = $\frac{100}{50.9} \times 24.02$

= 39.442 gm

Amount of coke required in the mixture = $39.442 \times \frac{23.4536}{516.534}$ gm

= 1.7911 gm

Corrected ratio of Al_2O_3 = 12.4759Amount of Al_2O_3 required in the mixture = $12.4759 \times \frac{23.4536}{516.534}$ gm

= 0.5665 gm

Weight of CaSO_4 in 1 gm pellet =

$$= \frac{408.438}{516.534 + 39.442 + 12.4759} \times 1 \text{ gm}$$

$$= 0.7185 \text{ gm}$$

Weight of coke in 1 gm pellet = $\frac{39.442}{568.4519} \times 1$

= 0.06938 gm

 \therefore weight of S in 1 gm pellet = $0.06938 \times \frac{6.3}{100}$

= 0.004371 gm

 \therefore CaSO_4 equivalent to the above weight of S contained in coke in 1 gm pellet

$$= 0.004371 \times \frac{136.146}{32.06}$$

= 0.01856 gm

Table 8.3.45.

System XVIII.

3 Gypsum : 2 Coke : 0.1567 Al_2O_3 .
1400°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc 0.1N NaOH used	Sulphide tit- ration cc 0.1 N KBrO_3 used
Wt. of boat = 6.0129 do. + pellet= 7.0917	1	44.7	17.35
Wt. of boat = 6.1614 do. + pellet= 7.2878	5	101.4	13.75
Wt. of boat = 5.8548 do. + pellet= 6.9262	10	96.55	13.35
Wt. of boat = 6.0177 do. + pellet= 7.0951	20	97.4	13.1

Observations:-

The pellets exfoliated on heating and were greyish brown in colour.

Table 8.3.46.

System XVIII.

3 Gypsum : 2 Coke : 0.1567 Al_2O_3 .

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.7185 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.01856 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurisation of CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correct- ed (a-b)			
1	1.0788	0.7751	0.3043	0.0200	0.2843	36.679	0.06259	8.075
5	1.1264	0.8093	0.6904	0.0209	0.6695	82.726	0.04961	6.130
10	1.0714	0.7698	0.6574	0.0199	0.6375	82.814	0.04816	6.256
20	1.0774	0.7741	0.6631	0.0200	0.6431	83.077	0.04726	6.105

Table 8.3.47.

System XVIII.

3 Gypsum : 2 Coke : 0.1567 Al_2O_3 .

1100°C.

Weights (gm)	Size (mts)	H_2SO_4 tit- ration cc 0.1 N NaOH used	Sulphide tit- ration cc 0.1 N KBrO_3 used
Wt. of boat = 6.0126 do. + pellet= 7.1309	1	2.3	9.75
Wt. of boat = 6.1615 do. + pellet= 7.2212	5	29.5	30.0
Wt. of boat = 5.8550 do. + pellet= 6.9098	10	59.0	32.8
Wt. of boat = 6.0180 do. + pellet= 7.1071	20	93.35	16.5

Observations:-

Same as in system VII at 1100°C.

Table 8.3.48.

System XVIII.

3 Gypsum : 2 Coke : 0.1567 Al_2O_3 .

1100°C.

Weight of CaSO_4 in 1 gm pellet = 0.7185 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.01856 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S. in coke (b)	Correct- ed (a-b)			
1	1.1183	0.8035	0.0157	S was un- burnt	0.0157	1.954	0.03518	4.378
5	1.0597	0.7614	0.2008	0.0197	0.1811	23.785	0.1082	14.211
10	1.0548	0.7579	0.4017	0.0196	0.3821	50.416	0.1183	15.609
20	1.0891	0.7825	0.6356	0.0202	0.6154	78.645	0.05953	7.608

3 Gypsum + 2 Coke + Al_2O_3

1400°C. ○

1100°C. Δ

(Nitrogen Atmosphere)

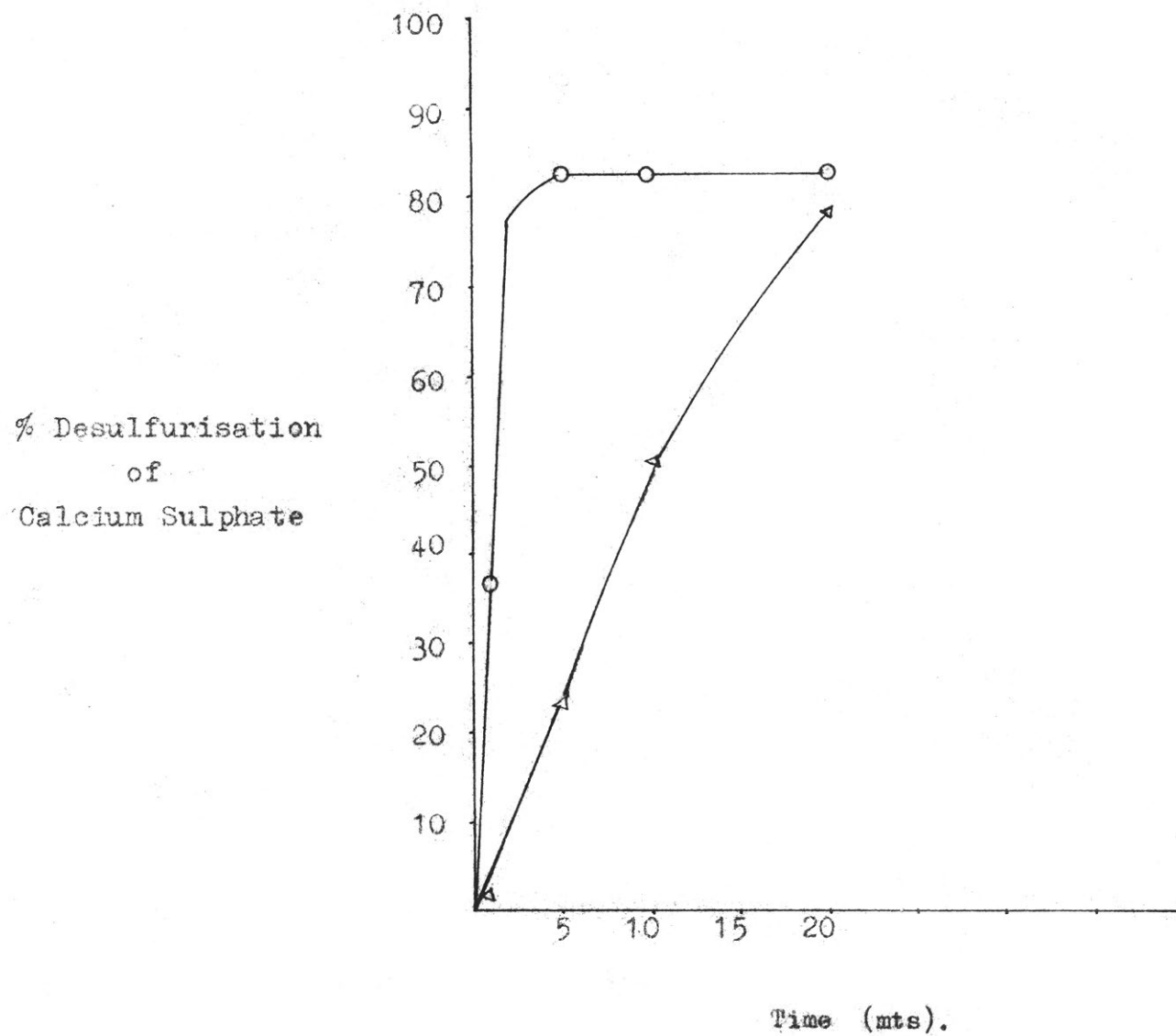


Fig.8.3.26

SYSTEM XVIII.

3 Gypsum : 2 Coke : 0.1567 Al_2O_3 .

1100°C.

(Nitrogen Atmosphere)

CaS formed in the system.

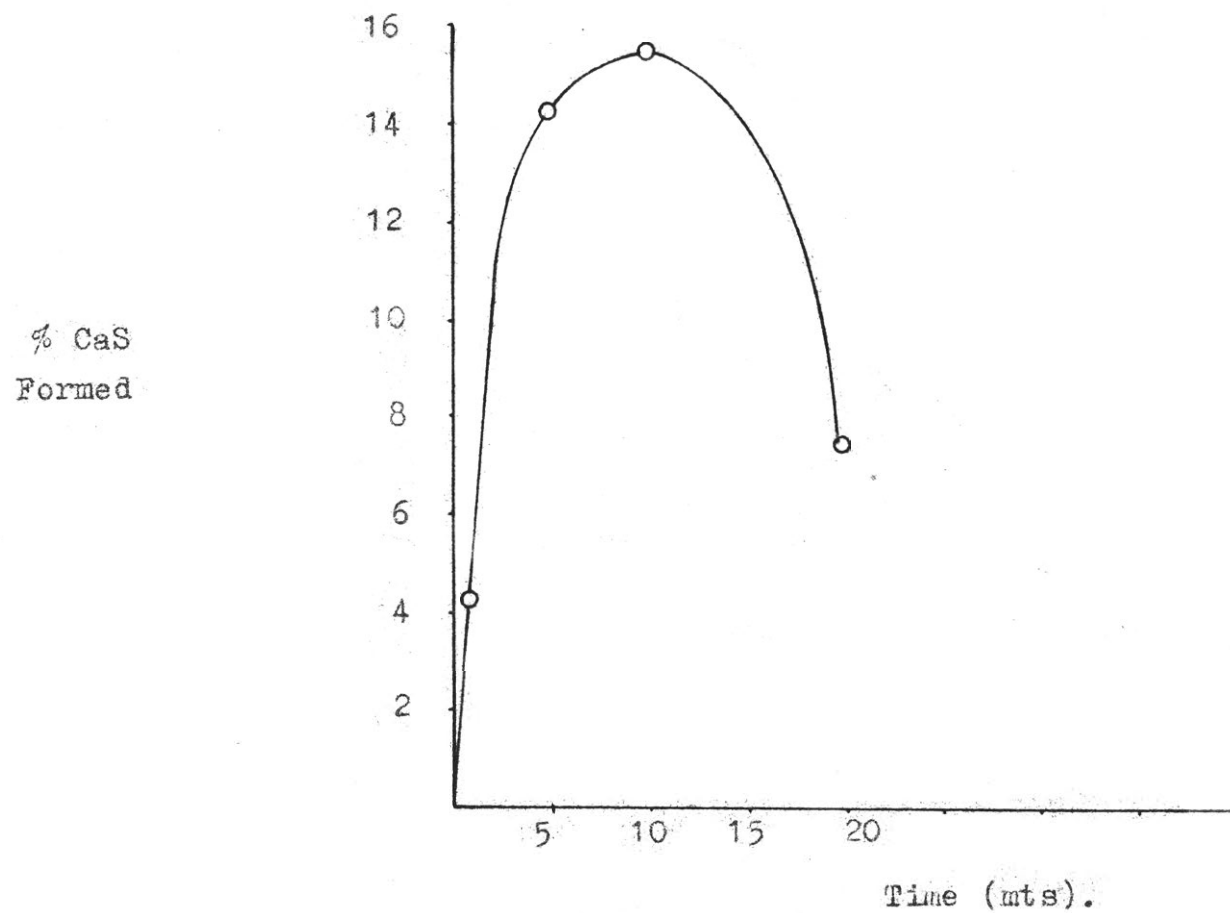


Fig. 8.3.27

System XIX.

3 Gypsum : 2 Coke : 0.04501 Fe_2O_3 Weight of CaSO_4 taken = 20.6350 gm.

$$\begin{aligned}\text{Corrected ratio of coke} &= \frac{100}{60.9} \times 24.02 \\ &= 39.442\end{aligned}$$

$$\begin{aligned}\therefore \text{Amount of coke required in the mixture} &= 39.442 \times \frac{20.6350 \text{ gm}}{516.534} \\ &= 1.5757 \text{ gm.}\end{aligned}$$

Corrected ratio of Fe_2O_3 = 4.1019

$$\begin{aligned}\therefore \text{Amount of } \text{Fe}_2\text{O}_3 \text{ required in the mixture} &= 4.1019 \times \frac{20.6350}{516.534} \text{ gm} \\ &= 0.1639 \text{ gm.}\end{aligned}$$

$$\begin{aligned}\text{Weight of } \text{CaSO}_4 \text{ in 1 gm pellet} &= \frac{408.438}{516.534 + 39.442 + 4.1019} \times 1 \text{ gm} \\ &= 0.7425 \text{ gm.}\end{aligned}$$

$$\begin{aligned}\text{Weight of coke in 1 gm pellet} &= \frac{39.442}{550.0779} \times 1 \\ &= 0.0717 \text{ gm.}\end{aligned}$$

$$\begin{aligned}\text{Weight of S in 1 gm pellet} &= 0.0717 \times \frac{6.3}{100} \\ &= 0.004517 \text{ gm.}\end{aligned}$$

$$\begin{aligned}\therefore \text{CaSO}_4 \text{ equivalent to the above weight of S contained} \\ \text{in 1 gm pellet} &= 0.004517 \times \frac{136.146}{32.06} \text{ gm} \\ &= 0.01918 \text{ gm.}\end{aligned}$$

Table 8.3.49

SystemXIX.

3 Gypsum : 2 Coke : 0.4501 Fe_2O_3
1400°C.

Weights	Time (mts)	H_2SO_4 tit- ration cc 0.1N NaOH used	Sulphide tit- ration cc 0.1 N KBrO_3 used
Wt. of boat = 5.9357	1	46.6	18.4
do. + pellet= 6.9357			
Wt. of boat = 5.7593	5	95.1	11.35
do. + pellet= 6.7973			
Wt. of boat = 5.8436	10	95.5	10.6
do. + pellet =6.8830			
Wt. of boat = 5.8386	20	91.05	9.9
do. + pellet= 6.8292			

Observations:

The pellets on heating became exfoliated and developed brown colour.

Table 8.3.50.

System XIX.

3 Gypsum : 2 Coke : 0.04501 Fe_2O_3 .

1400°C.

Weight of CaSO_4 in 1 gm pellet = 0.7425 gm. CaSO_4 equivalent to the wt. of S contained in coke
in 1 gm pellet = 0.01918 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm) Total CaSO_4 equiv- (a) alent to the wt. of S in coke (b)	Correct- ed (a-b)	% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
1	1.0000	0.7425	0.3173 0.0192	0.2981	40.148	0.06638	8.940
5	1.0380	0.7707	0.6475 0.0199	0.6276	81.432	0.04095	5.313
10	1.0394	0.7718	0.6502 0.0199	0.6303	81.666	0.03824	4.955
20	0.9906	0.7355	0.6199 0.0190	0.6009	81.700	0.03572	4.857

Table 8.3.51

System XIX.

3 Gypsum : 2 Coke : 0.04501 Fe_2O_3
 1100°C.

Weights	Time (mts)	H_2SO_4 tit- ration cc 0.1N NaOH used	Sulphide tit- ration cc 0.1N KBrO_3 used
Wt. of boat = 6.0118 do. + pellet= 7.0392	1	2.65	11.15
Wt. of boat = 6.1592 do. + pellet= 7.1840	5	28.9	32.5
Wt. of boat = 6.1591 do. + pellet= 7.2402	10	60.3	29.6
Wt. of boat = 6.0150 do. + pellet= 7.0890	20	92.2	16.0

Observations:-

The pellets were greyish white in colour and contained unburnt coke in 1 minute reading. Therefore the sulphur content of the coke was not accounted for in this case.

Table 8.3.52.

System XIX

3 Gypsum : 2 Coke : 0.04501 Fe_2O_3

1100°C.

Wt. of CaSO_4 in 1 gm pellet = 0.7425 gm. CaSO_4 equivalent to the wt. of S contained in coke in 1 gm pellet = 0.01918 gm.

Time (mts)	Weight of pellet (gm)	Weight of CaSO_4 in pellet (gm)	Weight of Desulfurised CaSO_4 (gm)			% Desulfurised CaSO_4	Weight of CaS formed (gm)	% CaS formed
			Total (a)	CaSO_4 equiv- alent to the wt. of S in coke (b)	Correc- ted (a-b)			
1	1.0274	0.7628	0.0180	S was un- burnt	0.0180	2.360	0.04023	5.274
5	1.0248	0.7609	0.1968	0.0197	0.1771	23.275	0.1173	15.416
10	1.0811	0.8027	0.4105	0.0207	0.3898	48.561	0.1068	13.305
20	1.0740	0.7974	0.6277	0.0206	0.6071	76.135	0.05772	7.239

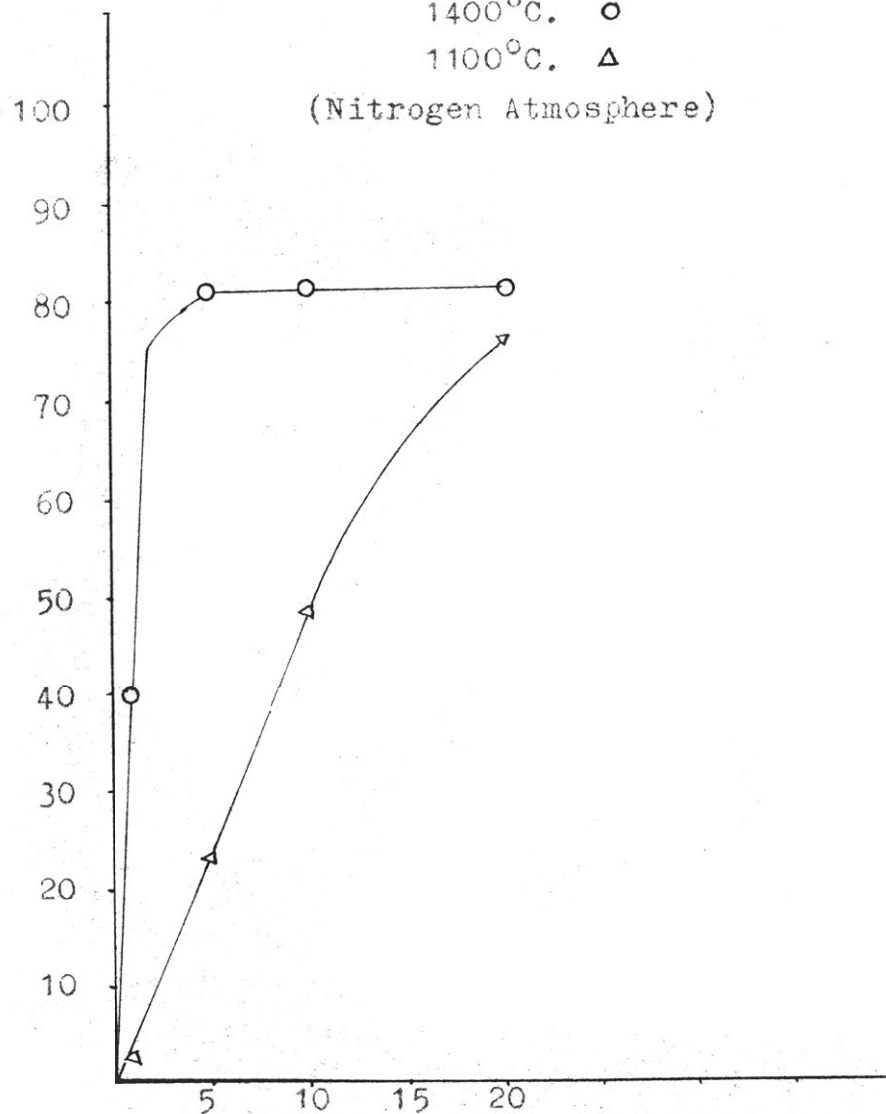
SYSTEM XIX.
3 Gypsum + 2 Coke + 0.04501 Fe_2O_3

1400°C. ○

1100°C. Δ

(Nitrogen Atmosphere)

% Desulfurisation
of
Calcium Sulphate



Time (mts).

Fig. 8.3.28

SYSTEM XIX.

3 Gypsum : 2 Coke : 0.04501 Fe_2O_3 .
1100°C.

(Nitrogen Atmosphere)

CaS formed in the system.

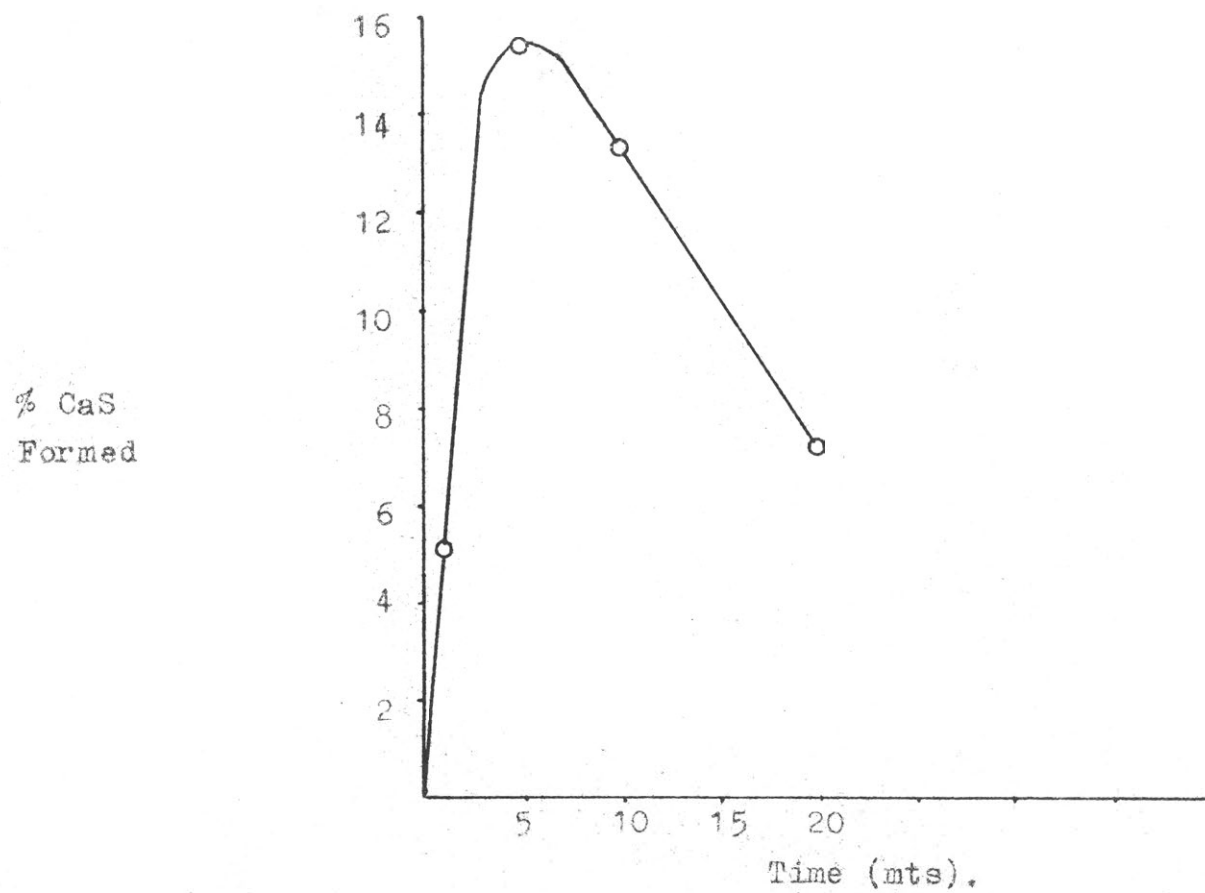


Fig. 8.3.29

System XX.

3 Gypsum : 1 CaS.

Weight of B.P.C. CaS taken = 3.5003 gm

Purity of B.P.C. CaS = 45.3%

CaSO₄ content of B.P.C. CaS = 37.411%

∴ CaSO₄·2H₂O equivalent to the CaSO₄ content
 of B.P.C. CaS = $37.411 \times \frac{172.178}{136.146}$

= 47.314%

Corrected ratio of B.P.C. CaS = $72.146 \times \frac{100}{45.3}$
 = 159.263

Additional weight of gypsum required in the
 mixture = $\left(\frac{516.534}{159.263} \times 3.5003 \right) - \left(\frac{47.314}{100} \times 3.5003 \right)$ gm
 = 9.6964 gm

Wt. of total sulphur in 1 gm pellet

$$= \frac{96.18 + 32.06}{\left[516.534 - \left(159.263 \times \frac{47.314}{100} \right) \right] + 159.263} \text{ gm}$$

$$= \frac{128.24}{600.4433} \text{ gm}$$

$$= 0.2136 \text{ gm}$$

Wt. of CaS in 1 gm pellet = $\frac{72.146}{600.4433}$
 = 0.1202 gm.

Table 8.3.53.
System XX.
3 Gypsum : 1 CaS.
1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1 N NaOH used	Sulphide titration cc 0.1 N KBrO ₃ used
Wt. of boat = 6.1502	1	43.4	20.25
do. + pellet= 7.2115			
Wt. of boat = 5.8254	5	125.7	nil
do. + pellet= 6.9012			
Wt. of boat = 6.0066	10	132.2	nil
do. + pellet= 7.0659			
Wt. of boat = 5.9570	20	141.0	nil
do. + pellet= 7.0389			

Observations:-

No melts were obtained.

Table 8.3.54.

System XX.

3 Gypsum : 1 CaS

1400°C.

Total sulphur in 1 gm pellet = 0.2136 gm.

Wt. of CaS in 1 gm pellet = 0.1202 gm.

Time (mts)	Weight of pellet (gm)	Weight of total sulfur in pellet (gm)	Weight of evolved sulfur (gm)	% Desulfurisation	Weight of CaS in pellet (gm)	Weight of CaS left behind (gm)	% CaS left behind
1	1.0613	0.2267	0.0695	30.657	0.1276	0.07306	57.257
5	1.0758	0.2298	0.2012	87.554	0.1293	nil	nil
10	1.0593	0.2263	0.2116	93.504	0.1273	nil	nil
20	1.0819	0.2311	0.2256	97.620	0.1300	nil	nil

SYSTEM AA.
3 Gypsum : 1 CaS.

1400°C.

(Nitrogen Atmosphere)

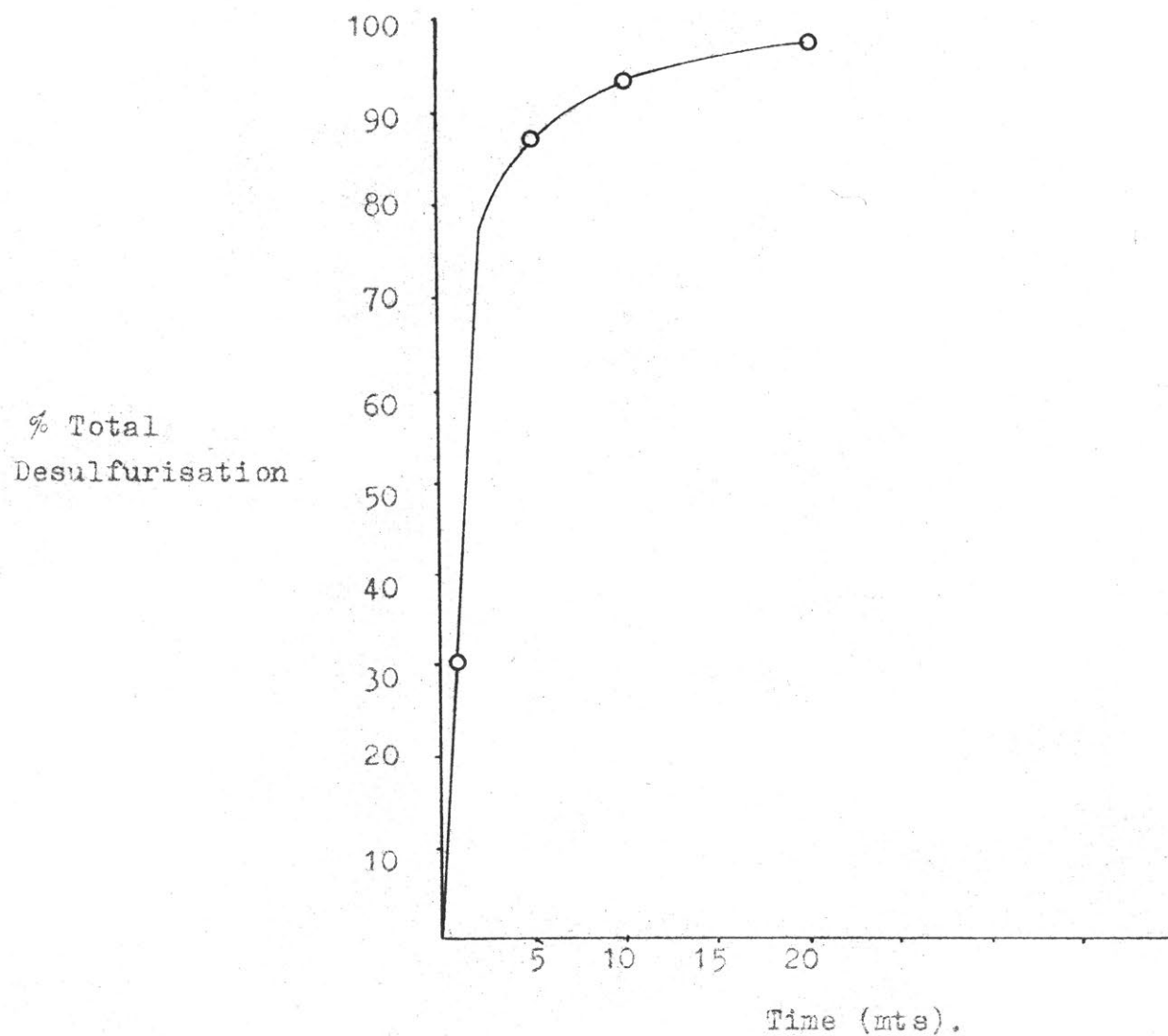


Fig. 8.3.30

SYSTEM XXI.

3 Gypsum : 1 CaS : 4/3 SiO₂.

Wt. of B.P.C. CaS taken = 3.4991 gm

corrected ratio of B.P.C. CaS = $72.146 \times \frac{100}{45.3}$

= 159.263

Additional wt. of gypsum required in the mixture

$$= \left(\frac{516.534 \times 3.4991}{159.263} \right) - \left(\frac{47.314 \times 3.4991}{100} \right) \text{ gm}$$

= 9.6930 gm.

Corrected ratio of silica = $60.06 \times \frac{4}{3} = 80.08$ ∴ Wt. of SiO₂ required in the mixture

$$= \frac{80.08}{159.263} \times 3.4991 = 1.7593 \text{ gm.}$$

Wt. of total sulphur in 1 gm pellet

$$= \frac{96.18 + 32.06}{\left[516.534 - \left(159.263 \times \frac{47.314}{100} \right) \right] + 159.263 + 80.08} \text{ gm.}$$

$$= \frac{128.24}{680.5233} \text{ gm}$$

$$= 0.1884 \text{ gm.}$$

Wt. of CaS in 1 gm pellet = $\frac{72.146}{680.5233} = 0.106 \text{ gm.}$

Table 8.3.55.

System XII.

3 Gypsum : 1 CaS : $4/3$ SiO₂.
1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1N NaOH used	Sulphide titration cc 0.1 N KBrO ₃ used
Wt. of boat = 6.0432	1	83.55	3.85
do. + pellet= 6.9780			
Wt. of boat = 5.9176	5	95.8	nil
do. + pellet= 6.8123			
Wt. of boat = 5.8254	10	106.75	nil
do. + pellet= 6.7633			
Wt. of boat = 6.0050	20	106.95	nil
do. + pellet= 6.9386			

Observations:-

No melts were obtained.

Table 8.3.56.

System XXI.

3 Gypsum : 1 CaS : $4/3$ SiO₂.

1400°C.

Wt. of total S in 1 gm pellet = 0.1884 gm.

Wt. of CaS in 1 gm pellet = 0.106 gm.

Time (mts)	Weight of pellet (gm)	Weight of total sulfur in pellet (gm)	Weight of evolved sulfur (gm)	% Desulfurisation	Weight of CaS in pellet (gm)	Weight of CaS left behind (gm)	% CaS left behind
1	0.9348	0.1761	0.1337	75.923	0.09909	0.01389	14.018
5	0.8947	0.1686	0.1533	90.925	0.09484	nil	nil
10	0.9379	0.1767	0.1708	96.661	0.09942	nil	nil
20	0.9336	0.1759	0.1711	97.271	0.09896	nil	nil

System XIII.

3 Gypsum : 1 CaS : 0.2089 Al_2O_3 .

Wt. of B.P.C. CaS taken = 3.4979 gm

$$\begin{aligned}\text{Corrected ratio of B.P.C. CaS} &= 72.146 \times \frac{100}{45.3} \\ &= 159.263\end{aligned}$$

Additional wt. of gypsum required in the mixture

$$\begin{aligned}&= \left(\frac{516.534}{159.263} \times 3.4979 \right) - \left(\frac{47.314}{100} \times 3.4979 \right) \text{ gm} \\ &= 9.6897 \text{ gm}\end{aligned}$$

$$\text{Corrected ratio of } \text{Al}_2\text{O}_3 = 12.4759 \times \frac{4}{3} = 16.6345$$

Wt. of Al_2O_3 required in the mixture

$$\begin{aligned}&= \frac{16.6345}{159.263} \times 3.4979 \text{ gm} \\ &= 0.3652 \text{ gm}\end{aligned}$$

Wt. of total sulphur in 1 gm pellet

$$\begin{aligned}&= \frac{96.18 + 32.06}{\left[516.534 - \left(159.263 \times \frac{47.314}{100} \right) \right] + 159.263 + 16.6345} \text{ gm} \\ &= \frac{128.24}{617.0778} \text{ gm} \\ &= 0.2078 \text{ gm}\end{aligned}$$

$$\begin{aligned}\text{Wt. of CaS in 1 gm pellet} &= \frac{72.146}{617.0778} \\ &= 0.1169 \text{ gm}\end{aligned}$$

Table 8.3.57.

System XIII.

3 Gypsum : 1 CaS : 0.2089 Al_2O_3 .
 1400°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc 0.1 N NaOH used	Sulphide titration cc 0.1 N KBrO_3 used
Wt. of boat = 5.9564 do. + pellet = 7.1072	1	44.1	25.75
Wt. of boat = 6.1494 do. + pellet = 7.2730	5	127.95	nil
Wt. of boat = 5.8267 do. + pellet = 6.9162	10	132.95	nil
Wt. of boat = 6.0080 do. + pellet = 7.1310	20	143.3	nil

Observations:-

No melts were obtained.

Table 8.3.58.

System XXII.

3 Gypsum : 1 CaS : 0.2089 Al_2O_3
 1400°C.

Wt. of total sulphur in 1 gm pellet = 0.2076 gm.

Wt. of CaS in 1 gm pellet = 0.1169 gm.

Time (mts)	Weight of pellet (gm)	Weight of total sulfur in pellet (gm)	Weight of evolved sulfur (gm)	% Desulfurisation	Weight of CaS in pellet (gm)	Weight of CaS left behind (gm)	% CaS left behind
1	1.1508	0.2391	0.0706	29.527	0.1345	0.09290	69.071
5	1.1236	0.2335	0.2048	87.709	0.1313	nil	nil
10	1.0895	0.2264	0.2128	93.993	0.1274	nil	nil
20	1.1230	0.2334	0.2293	98.243	0.1313	nil	nil

System XXIII.

3 Gypsum : 1 CaS : 0.06 Fe₂O₃.

Wt. of B.P.C. CaS taken = 3.5052 gm.

Corrected ratio of B.P.C. CaS = 159.263

Additional wt. of gypsum required in the mixture

$$= \left(\frac{516.534}{159.263} \times 3.5052 \right) - \left(\frac{47.314}{100} \times 3.5052 \right)$$

$$= 9.7099 \text{ gm.}$$

$$\text{Corrected ratio of Fe}_2\text{O}_3 = 4.1019 \times \frac{4}{3} = 5.4692$$

∴ Wt. of Fe₂O₃ required in the mixture

$$= \frac{5.4692}{159.263} \times 3.5052 \text{ gm}$$

$$= 0.1204 \text{ gm.}$$

Wt. of total sulphur in 1 gm pellet

$$= \frac{96.18 + 32.06}{\left[516.534 - \left(159.263 \times \frac{47.314}{100} \right) \right] + 159.263 + 5.4692} \text{ gm}$$

$$= \frac{128.24}{605.9125}$$

$$= 0.2116 \text{ gm.}$$

Wt. of CaS in 1 gm pellet = $\frac{72.146}{605.9125}$

$$= 0.1191 \text{ gm}$$

Table 8.3.59

System XXIII.

3 Gypsum : 1 CaS : 0.06 Fe_2O_3 .

1400°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc 0.1 N NaOH used	Sulphide titration cc 0.1 N KBrO_3 used
Wt. of boat = 6.0403 do. + pellet= 7.1067	1	59.25	19.25
Wt. of boat = 5.9166 do. + pellet= 6.9606	5	120.75	nil
Wt. of boat = 5.9556 do. + pellet= 7.0856	10	140.45	nil
Wt. of boat = 5.7510 do. + pellet= 6.8210	20	137.5	nil

Observations:-

No melts were obtained.

Table 8.3.60.

System XXIII.

3 Gypsum : 1 CaS : 0.06 Fe₂O₃.
1400°C.

Wt. of total S in 1 gm pellet = 0.2116 gm.

Wt. of CaS in 1 gm pellet = 0.1191 gm.

Time (mts)	Weight of pellet (gm)	Weight of total sulfur in pellet (gm)	Weight of evolved sulfur (gm)	% Desulfurisation	Weight of CaS in pellet (gm)	Weight of CaS left behind (gm)	% CaS left behind
1	1.0664	0.2257	0.0948	42.003	0.1270	0.06945	54.685
5	1.0440	0.2209	0.1932	87.460	0.1243	nil	nil
10	1.1300	0.2391	0.2248	94.0192	0.1346	nil	nil
20	1.0700	0.2264	0.2200	97.173	0.1274	nil	nil

SYSTEM XXI. 3 Gypsum : 1 CaS : 4/3/SiO₂ ○
 SYSTEM XXII. 3 Gypsum : 1 CaS : 0.2089 Al₂O₃ □
 SYSTEM XXIII. 3 Gypsum : 1 CaS : 0.06 Fe₂O₃ △
 1400°C.

(Nitrogen Atmosphere)

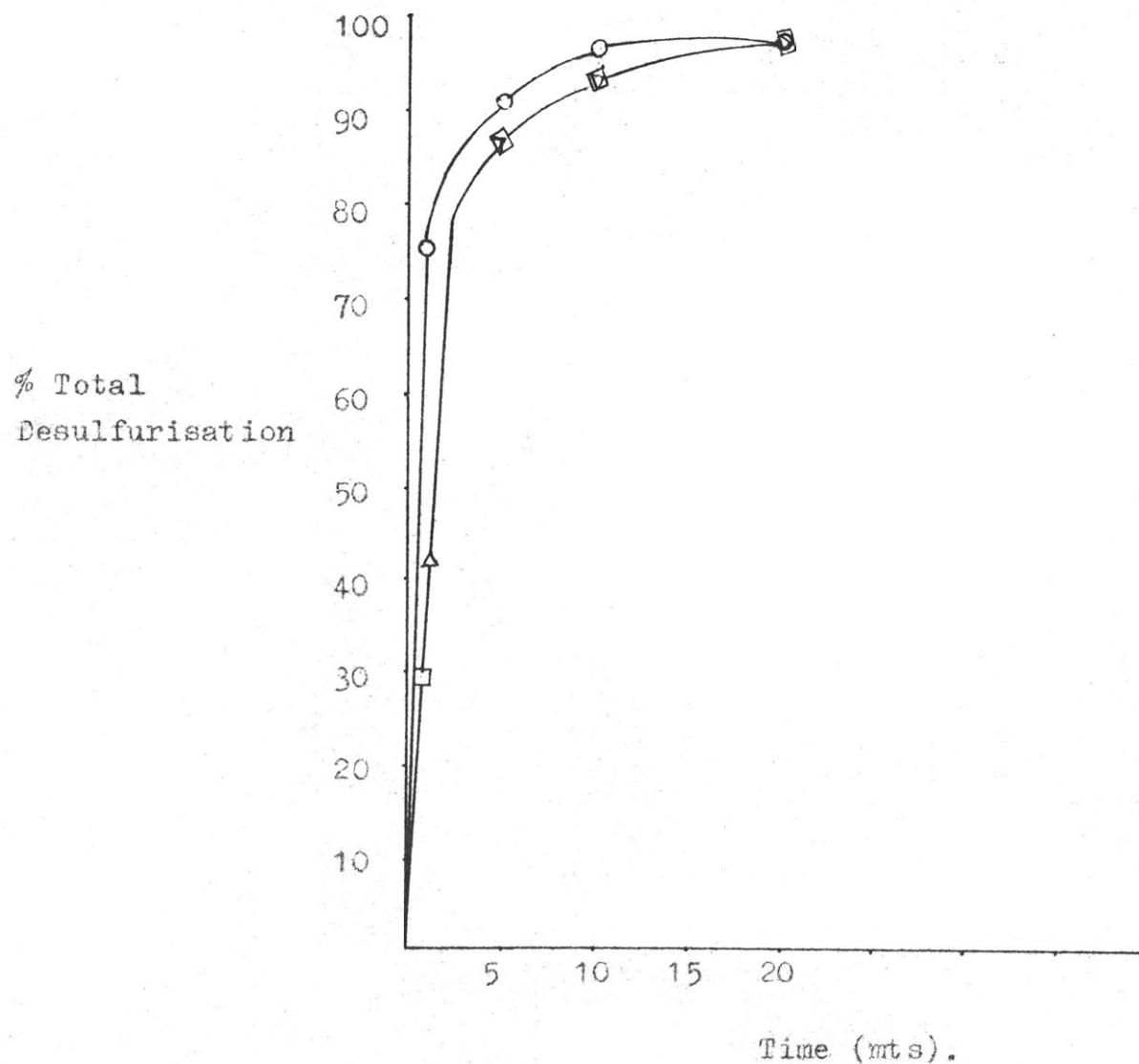


Fig. 8.3.31

System XXIV.

3 Gypsum : 0.425 CaS.

Wt. of B.P.C. CaS taken = 3.3914 gm.

Purity of B.P.C. CaS = 45.3%

 CaSO_4 content of B.P.C. CaS = 37.411% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ equivalent to the CaSO_4 content of theB.P.C. CaS = $37.411 \times \frac{172.178}{136.146}$

136.146

= 47.314%

0.425 gram molecules of CaS = 0.425×72.146

= 30.6621 gm CaS

∴ Corrected ratio of B.P.C. CaS = $30.6621 \times \frac{100}{45.3}$

45.3

= 67.6868

Additional wt. of gypsum to be weighed

$$= \left(\frac{516.534}{67.6868} \times 3.3914 \right) - \left(\frac{47.314}{100} \times 3.3914 \right) \text{ gm}$$

= 24.2759 gm.

Wt. of total sulphur in 1 gm pellet

$$= \frac{96.18 + (32.06 \times 0.425)}{\left[516.534 - \left(67.6868 \times \frac{47.314}{100} \right) \right] + 67.6868} \text{ gm}$$

= $\frac{109.8055}{552.1955}$

552.1955

= 0.1989 gm.

Wt. of CaS in 1 gm pellet = $\frac{30.6621}{552.1955}$

552.1955

= 0.0555 gm.

Table 8.3.61.

System XXIV.

3 Gypsum : 0.425 CaS.

1400°C.

Weights (gm)	Time (mts)	H ₂ SO ₄ tit- ration cc 0.1 N NaOH used	Sulphide titration cc 0.1 N KBrO ₃ used
Wt. of boat = 6.0126 do. + pellet= 7.1040	1	26.65	8.35
Wt. of boat = 5.1616 do. + pellet= 7.2821	5	62.6	0.5
Wt. of boat = 5.8579 do. + pellet= 7.0072	10	71.9	nil
Wt. of boat = 6.0181 do. + pellet= 7.1861	20	86.3	nil

Observations:-

The pellets did not melt and were white in colour after heating.

Table 8.3.62.

System XXIV.

3 Gypsum : 0.425 CaS.

1400°C.

Wt. of total S in 1 gm pellet = 0.1989 gm.

Wt. of CaS in 1 gm pellet = 0.0555 gm.

Time (mts)	Weight of pellet (gm)	Weight of total S in pellet (gm)	Weight of evolved sulfur (gm)	% Desulfurisation	Weight of CaS in pellet (gm)	Weight of CaS left behind (gm)	% CaS left behind
1	1.0914	0.2171	0.0426	19.622	0.06057	0.03012	49.728
5	1.1205	0.2229	0.1002	44.953	0.06219	0.001804	2.901
10	1.1493	0.2286	0.1151	50.350	0.06379	nil	nil
20	1.1680	0.2323	0.1381	59.449	0.06482	nil	nil

3 Gypsum : 0.425 CaS.
1400°C.
(Nitrogen Atmosphere)

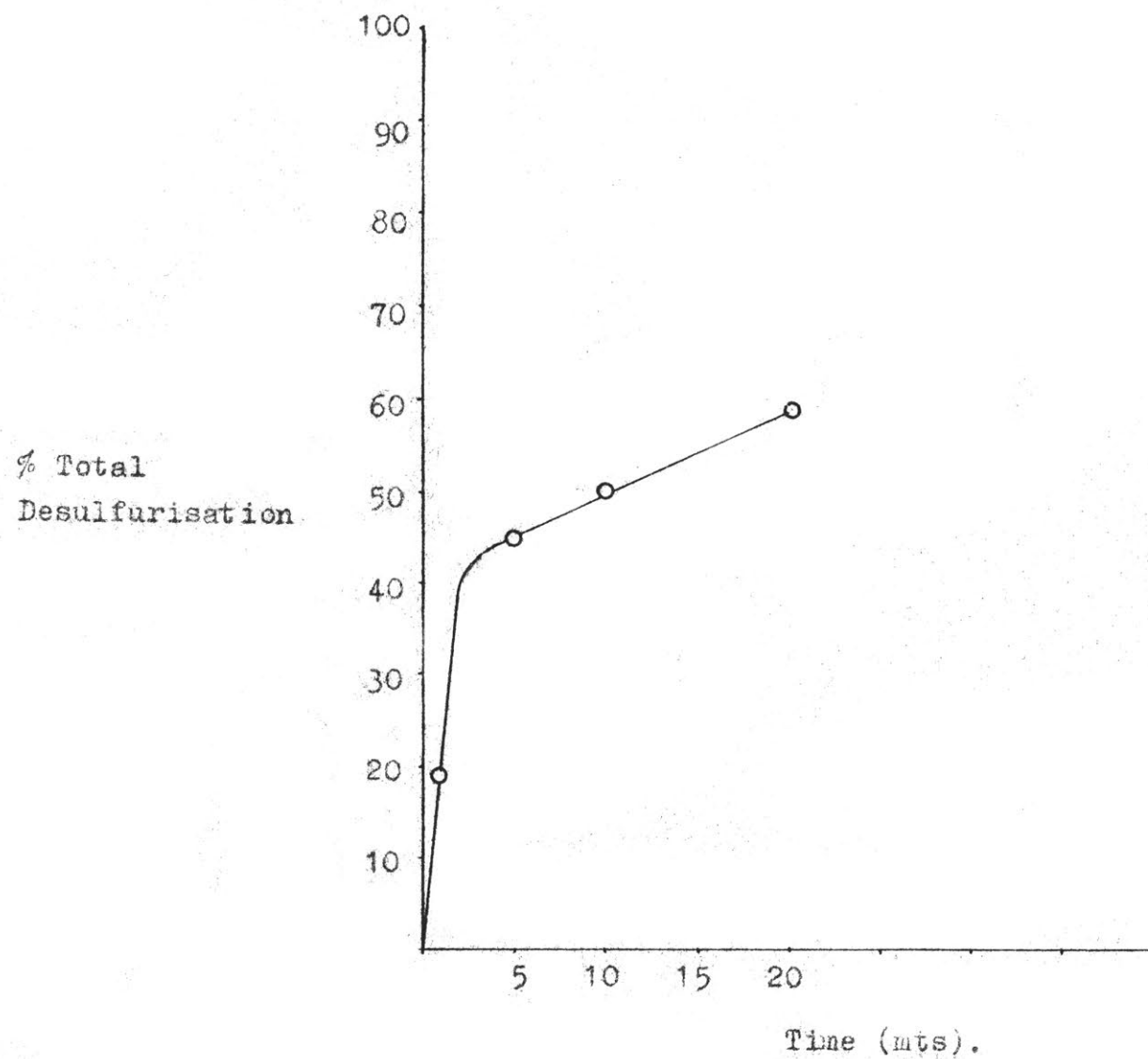


Fig. 8.3.32

System XXV.

$$3 \text{ Gypsum} : 0.425 \text{ CaS} : 1.251 \text{ SiO}_2$$

$$\text{Wt. of B.P.C. CaS taken} = 1.6758 \text{ gm.}$$

$$0.425 \text{ gm molecules of CaS} = 0.425 \times 72.146 = 30.6621 \text{ gm CaS}$$

$$\therefore \text{Corrected ratio of B.P.C. CaS} = 30.6621 \times \frac{100}{45.3} = 67.6868$$

Additional wt. of gypsum to be weighed

$$= \left(\frac{516.534}{67.6868} \times 1.6758 \right) - \left(\frac{47.314}{100} \times 1.6758 \right) \text{ gm}$$

$$= 11.9955 \text{ gm.}$$

$$\text{Corrected ratio of silica} = 60.06 \times 1.251$$

$$= 75.135$$

Weight of silica required in the mixture

$$= \frac{75.135}{67.6868} \times 1.6758 \text{ gm}$$

$$= 1.8602 \text{ gm.}$$

Wt. of total S in 1 gm pellet

$$= \frac{96.18 + (32.06 \times 0.425)}{\left[\frac{516.534}{67.6868} - \left(\frac{47.314}{100} \times \frac{67.6868}{100} \right) \right] + 67.6868 + 75.135} \text{ gm}$$

$$= \frac{109.8055}{627.3305}$$

$$= 0.1750 \text{ gm.}$$

$$\text{Wt. of CaS in 1 gm pellet} = \frac{30.6621}{627.3305}$$

$$= 0.0489 \text{ gm.}$$

Table 8.3.63
 System XIV.
 3 Gypsum : 0.425 CaS : 1.251 SiO₂.
 1400°C.

Weights (gm)	Time (mins)	H ₂ SO ₄ tit- ration cc 0.1 N NaOH used	Sulphide titration cc 0.1 N KBrO ₃ used
Wt. of boat = 6.0126 do. + pellet= 7.0278	1	41.5	1.9
Wt. of boat = 6.1596 do. + pellet= 7.1479	5	56.9	nil
Wt. of boat = 5.8492 do. + pellet= 6.8595	10	67.0	nil
Wt. of boat = 6.0152 do. + pellet= 7.0204	20	76.0	nil

Observations:-

Melts were obtained in the boat after 5 minutes heating and over.

Table 8.3.54.

System XXV.

3 Gypsum : 0.425 CaS : 1.251 SiO₂.
1400°C.

Wt. of total S in 1 gm pellet = 0.1750 gm.

Wt. of CaS in 1 gm pellet = 0.0489 gm.

Time (mts)	Weight of pellet (gm)	Weight of total sulfur in pellet (gm)	Weight of evolved sulfur (gm)	% Desulfurisation	Weight of CaS in pellet (gm)	Weight of CaS left behind (gm)	% CaS left behind
1	1.0152	0.1777	0.0664	37.366	0.04964	0.006855	13.809
5	0.9883	0.1730	0.0911	52.659	0.04833	nil	nil
10	1.0103	0.1768	0.1072	60.633	0.04940	nil	nil
20	1.0092	0.1759	0.1216	69.130	0.04915	nil	nil

System XVI.

3 Gypsum : 0.425 CaS : 0.196 Al_2O_3 .

Wt. of B.P.C. CaS taken = 1.8650 gm.

0.425 gram molecules of CaS = 0.425×72.146
 = 30.6621 gram CaS.

∴ Corrected ratio of B.P.C. CaS = $30.6621 \times \frac{100}{45.3}$

= 67.6868

Additional weight of gypsum required in the mixture

$$= \left(\frac{516.534}{67.6868} \times 1.8650 \right) - \left(\frac{47.314}{100} \times 1.8650 \right) \text{ gm}$$

= 13.3498 gm.

Corrected ratio of Al_2O_3 = 12.4759×1.251
 = 15.6074

Weight of Al_2O_3 required in the mixture

$$= \frac{15.6074 \times 1.8650}{67.6868} \text{ gm}$$

= 0.43 gm.

Weight of total sulphur in 1 gm pellet

$$= \frac{96.18 + (32.06 \times 0.425)}{\left[\frac{516.534 - \left(67.6868 \times \frac{47.314}{100} \right)}{100} \right] + 67.6868 + 15.6074}$$

= 109.8055

567.8029

= 0.1934 gm.

Weight of CaS in 1 gm pellet = 30.6621 gm

567.8029

= 0.0540 gm.

Table 8.3.65

System XVI.

3 Gypsum : 0.425 CaS : 0.196 Al_2O_3 .
 1400°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- con. ration 0.1 N NaOH used	Sulphide titration cc 0.1 N KBrO_3 used
Wt. of boat = 6.0466 do. + pellet = 7.1872	1	25.6	8.15
Wt. of boat = 5.9364 do. + pellet = 7.0276	5	56.65	nil
Wt. of boat = 5.7600 do. + pellet = 6.8762	10	65.55	nil
Wt. of boat = 5.8436 do. + pellet = 6.9756	20	78.6	nil

Observations:-

Melts were obtained in the boats after 5 minutes heating and over.

Table 8.3.66.

System XXVI.

3 Gypsum : 0.425 CaS : 0.196 Al_2O_3 .

1400°C.

Wt. of total S in 1 gm pellet = 0.1934 gm.

Wt. of CaS in 1 gm pellet = 0.0540 gm.

Time (mts)	Weight of pellet (gm)	Weight of total sulfur in pellet (gm)	Weight of evolved sulfur (gm)	% Desulfurisation	Weight of CaS in pellet (gm)	Weight of CaS left behind (gm)	% CaS left behind
1	1.1406	0.2206	0.0410	18.586	0.06159	0.0294	47.735
5	1.0912	0.2110	0.0307	42.986	0.05892	nil	nil
10	1.1162	0.2159	0.1049	48.587	0.06027	nil	nil
20	1.1320	0.2189	0.1258	57.470	0.06113	nil	nil

System XIVII.

3 Gypsum : 0.425 CaS : 0.0563 Fe_2O_3 .

Wt. of B.P.C. CaS taken = 2.1353 gm.

0.425 gram molecules of CaS = 0.425×72.146
 = 30.6621 gram CaS

Corrected ratio of B.P.C. CaS = $\frac{30.6621 \times 100}{45.3}$
 = 67.6868

Additional wt. of gypsum required in the mixture

$$= \left(\frac{516.534}{67.6868} \times 2.1353 \right) - \left(\frac{47.314}{100} \times 2.1353 \right) \text{ gm.}$$

$$= 15.2846 \text{ gm.}$$

Corrected ratio of Fe_2O_3 = 5.4692×1.251
 = 6.842 gm.

Wt. of Fe_2O_3 required in the mixture = $\frac{6.842 \times 2.1353}{67.6868}$ gm.
 = 0.2158 gm.

Wt. of total sulphur in 1 gm pellet

$$= \frac{96.18 + (32.06 \times 0.425)}{\left[516.534 - \left(67.6868 \times \frac{47.314}{100} \right) \right] + 67.6868 + 6.842}$$

$$= \frac{109.8055}{559.0375}$$

$$= 0.1964 \text{ gm.}$$

Wt. of CaS in 1 gm pellet = $\frac{30.6621}{559.0375}$
 = 0.0548 gm.

Table 8.3.67.

System XXVII.

3 Gypsum : 0.425 CaS : 0.0563 Fe_2O_3 .
1400°C.

Weights (gm)	Time (mts)	H_2SO_4 tit- ration cc 0.1 N NaOH used	Sulphide titration cc 0.1 N KBrO_3 used
Wt. of boat = 6.1547 do. + pellet= 7.2510	1	35.2	5.55
Wt. of boat = 5.8418 do. + pellet= 6.9706	5	62.9	nil
Wt. of boat = 5.8378 do. + pellet= 6.9301	10	70.1	nil
Wt. of boat = 5.9858 do. + pellet = 7.1264	20	85.7	nil

Observations:-

Brown melts were obtained in the boats after
5 minutes heating and over.

Table 8.3.68.

System XXVII.

3 Gypsum : 0.425 CaS : 0.0563 Fe_2O_3 .

1400°C.

Wt. of total S in 1 gm pellet = 0.1964 gm.

Wt. of CaS in 1 gm pellet = 0.0548 gm.

Time (mts)	Weight of pellet (gm)	Weight of total sulfur in pellet (gm)	Weight of evolved sulfur (gm)	% Desulfurisation	Weight of CaS in pellet (gm)	Weight of CaS left behind (gm)	% CaS left behind
1	1.0963	0.2153	0.0563	26.150	0.06008	0.0200	33.289
5	1.1288	0.2217	0.1007	45.422	0.06186	nil	nil
10	1.0923	0.2145	0.1122	52.308	0.05986	nil	nil
20	1.1406	0.2240	0.1371	61.205	0.06250	nil	nil

SYSTEM XXV. 3 Gypsum : 0.425 CaS : 0.196 Al_2O_3 \square
 SYSTEM XXVI. 3 Gypsum : 0.425 CaS : 0.0563 Fe_2O_3 \triangle

1400°C.

(Nitrogen Atmosphere)

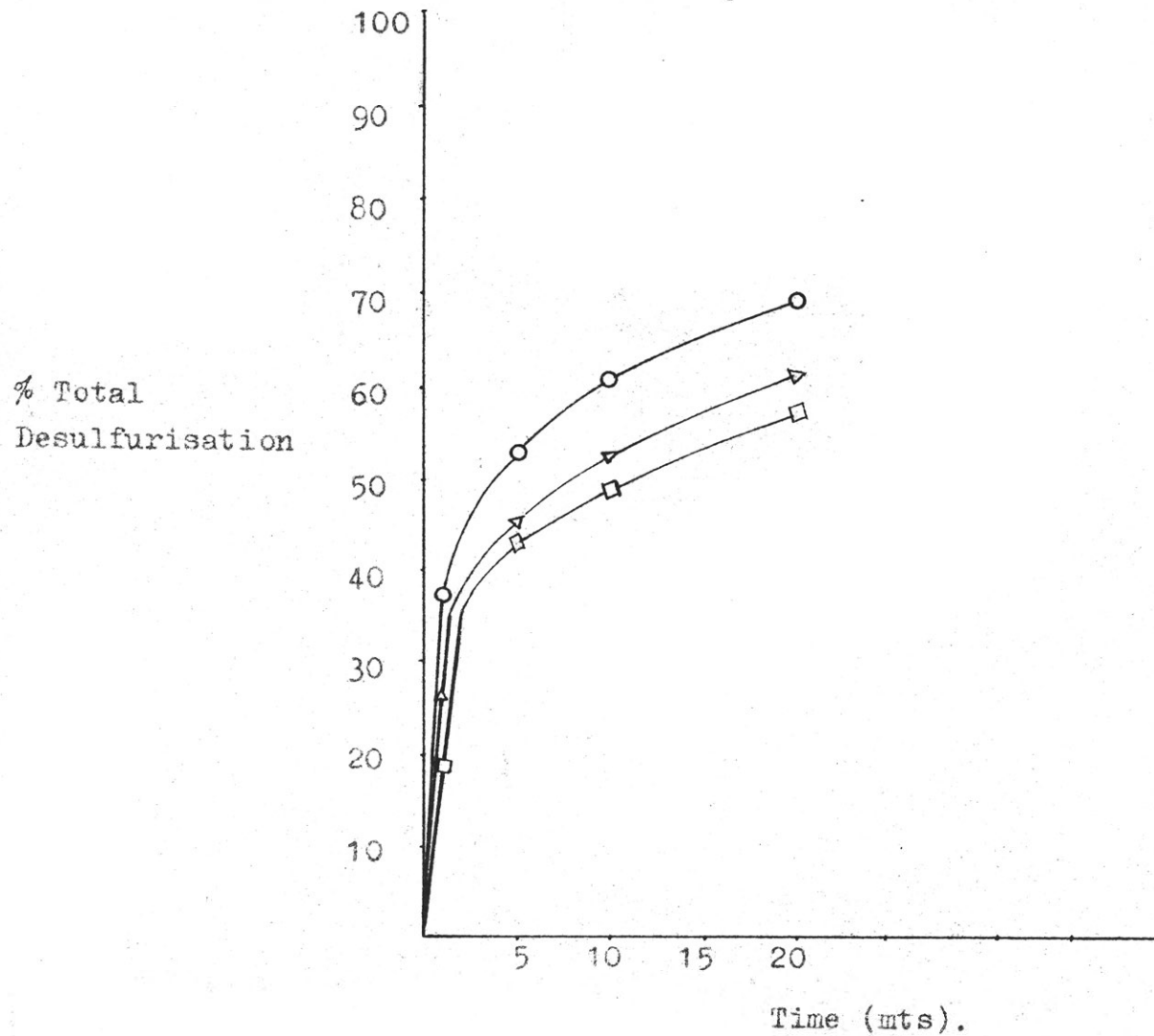


Fig. 8.3.33

C. Proof of the Active Desulphurisation of Calcium Sulphate by Carbon:-

To prove the active desulphurisation of calcium sulphate by carbon and account for the low slope of desulphurisation curve, after it was burnt off, the following procedures were adopted --

(1) Four Weighed Pellets of the System XIII were heated at 1400°C . for 20 minutes and the percentage desulphurisation for the combined weight was noted. After calculating the weight of the material left in the boats, it was removed from the boats and again weighed. The weight of the undecomposed calcium sulphate in this material was computed and mixed with pure carbon in the ratio $3 \text{ CaSO}_4 : 2 \text{ C}$. A pellet struck from this mixture was weighed, and the weight of CaSO_4 in it was calculated. The pellet was heated in the reactor in oxidising atmosphere for 20 minutes and desulphurisation was noted. From this value the percentage desulphurisation of the amount of CaSO_4 left in the material, after original 20 minutes heating, was calculated.

The point representing the combined desulphurisation of CaSO_4 (with the coke already contained in the mixture and with pure carbon) was plotted on the graph of System XIII, along with the point, representing the desulphurisation of CaSO_4 , after the initial 20 minutes heating. They show clearly the active desulphurisation of CaSO_4 by carbon.

Calculations:-

Total weight of pellets = 3.8507 gm

Weight of CaSO_4 in the pellets = 2.4860 gm

Total volume of N/10 NaOH used = 320.75 cc

= 2.1838 gm total desulphurised CaSO_4

Correcting for the sulphur contained in the coke, the actual amount of CaSO_4 desulphurised = 2.1838 - 0.0642
= 2.1196 gm.

Desulphurisation after the initial 20 minutes heating
= $\frac{2.1196 \times 100}{2.4860}$
= 85.261%

Weight of the material left behind in the boats
= 1.4690 gm.

Weight of undesulphurised CaSO_4 in this material
= $\frac{2.486 \times (100 - 85.261)}{100}$
= 0.3664 gm.

The material was scratched off from the boats, powdered and weighed.

Weight of powdered material = 1.2982 gm

Weight of CaSO_4 in this material = $1.2982 \times \frac{0.3664}{1.4690}$ gm
= 0.3238 gm.

Weight of pure carbon added to the above material
= $0.3238 \times \frac{24.02}{408.438}$
= 0.019 gm.

The mixture was made and a pellet was formed.

Weight of the pellet = 1.2166 gm.

$$\begin{aligned}\text{Weight of CaSO}_4 \text{ in the pellet} &= \frac{0.3238 \times 1.2166}{1.2982 + 0.019} \\ &= 0.299 \text{ gm.}\end{aligned}$$

The pellet was heated for 20 minutes at 1400°C. and the desulphurisation noted.

$$\begin{aligned}\text{Amount of 0.1N NaOH used} &= 37.1 \text{ cc.} \\ &= 0.2526 \text{ gm desulphurised} \\ &\quad \text{CaSO}_4.\end{aligned}$$

$$\begin{aligned}\therefore \text{Amount of CaSO}_4 \text{ which would be desulphurised in the} \\ \text{mixture containing 0.3664 gm CaSO}_4 &= \frac{0.2526}{0.299} \times 0.3664 \text{ gm} \\ &= 0.3097 \text{ gm.}\end{aligned}$$

$$\begin{aligned}\therefore \text{Total desulphurisation with the coke already con-} \\ \text{tained in the mixture and with pure carbon} \\ &= 2.1196 + 0.3097 \\ &= 2.4293 \text{ gm.}\end{aligned}$$

$$\begin{aligned}\therefore \% \text{ combined desulphurisation} &= \frac{2.4293}{2.486} \times 100 \\ &= 97.719\%\end{aligned}$$

Results:- Desulphurisation of CaSO_4 after the initial 20 minutes heating = 85.261%
Total desulphurisation of CaSO_4 with coked pure carbon = 97.719%

(11) After heating a pellet of System XIII for 20 minutes at 1400°C., the issuing gases were led through 100 cc of 50% chromic acid to scrub off SO_2 and then

through 100 cc of N/20 $\text{Ba}(\text{OH})_2$ solution. The strength of $\text{Ba}(\text{OH})_2$ remained unchanged even after one hour, showing the absence of CO_2 in the gases and hence the complete burning of the carbon contained in coke, before 20 minutes. The low slope of the desulphurisation curve, was therefore due to the elimination of carbon from the system.

d. Macroscopic examination of the action of carbon on gypsum.

Preparation of specimens:-

Two crystals of gypsum were selected and cut carefully parallel to the c axis, to fit into the platinum boats, keeping some space between the crystals and the sides of the boats. The thickness of the crystals was cut to 1/4th of an inch and the edges were evenly ground by grade 80-carborundum. They were then placed in the boats and surrounded by pure sugar charcoal on all sides.

The crystals were then heated in an atmosphere of Nitrogen at (1) 1400°C for one minute and (2) 1100°C for 5 minutes, to obtain maximum sulphide content, at each temperature and the sulphide prints obtained. The crystals swelled on heating due to the loss of water of crystallisation.

Sulphide Prints:-

Pieces of bromide photographic paper (matt

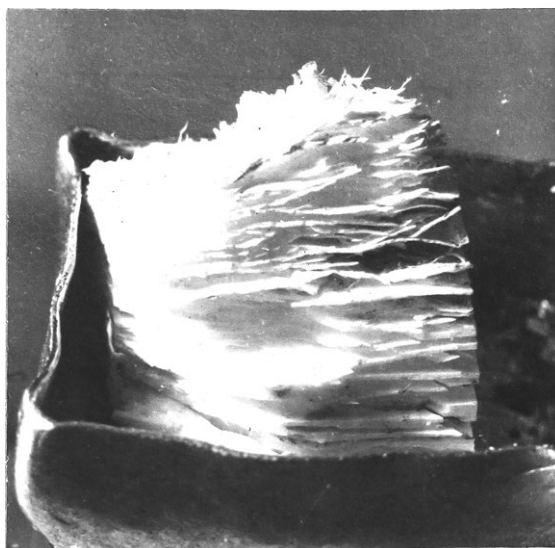


Fig. 8.3.34

Swelling and lamination of the gypsom
crystal after heating for one minute
at 1400°C.

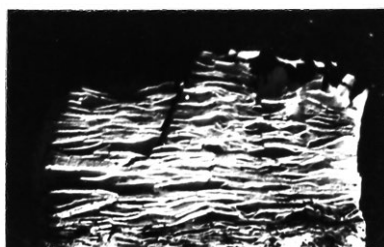


Fig. 8.3.35

Swelling and lamination of the gypsom
crystal after heating for 5 minutes
at 1100°C.

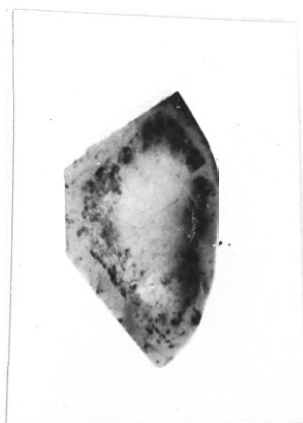


Fig. 8.3.36

Sulphide print of the gypsum crystal
after heating in carbon for one minute
at 1400°C .

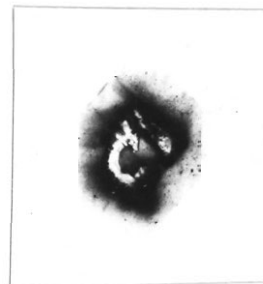
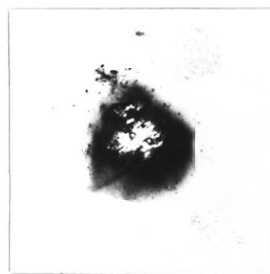


Fig. 8.3.37 (a)

Fig. 8.3.37 (b)

Sulphide prints of the gypsum crystal after heating in
carbon for 5 minutes at 1100°C .

surface) were soaked in a 3% solution of sulphuric acid in water for two minutes; longer time caused the gelatine to swell too much and become slippery. The paper was taken out of the acid and the excess of solution was removed with blotting paper, so that none remained except that which had been absorbed by the gelatine. The gypsum crystals were then laminated by a razor blade and the section carefully placed on the sensitised paper and pressed by a sheet of glass for 5 minutes. The sulphide in the pellet was attacked by the dilute acid evolving hydrogen sulphide gas which stained the bromide paper.

The sections of the specimens were removed and the paper was swilled in water for three minutes and immersed in 20% hypo solution for five minutes. It was then swilled in water for 20 minutes and dried. No dark room was required for the process.

The patterns obtained were photographically reproduced as shown.

CHAPTER IX.

Description and cost considerations of the proposed plant for the manufacture of sulphuric acid and cement from gypsum.

Note:- All available information about the British and German factories have been carefully checked before this chapter has been written.

I. Chemical Aspects:-

It is possible to decompose CaSO_4 by the mere application of heat. At 1375°C only 1.33% of undecomposed CaSO_4 is left, after the equilibrium has been reached. With carbon it is reduced to sulphide between 800° and 900°C . The temperature of incipient reaction of CaSO_4 with SiO_2 is about 870°C and the reaction is accelerated by the use of ferruginous sand, since iron oxide acts as a catalyst. Iron oxide is contained in coke and coal, and the balance can be supplied from any cheap source.

The temperature of incipient reaction of CaSO_4 with Al_2O_3 is $940^\circ - 950^\circ\text{C}$, and the reaction is accelerated by increase in temperature. With SiO_2 and Al_2O_3 , a total pressure of 76 cm of mercury is reached at temperatures of 1273°C and 1363°C respectively. The difference in temperatures is influenced by the different heats of formation of calcium silicate and calcium aluminates.

II. Production of sulphuric acid and cement on large scale:-

The following steps are necessary for the production of sulphuric acid and cement on a large scale:-

- (a) Production and preparation of raw materials.
- (b) Production of SO_2 containing gases.
- (c) Purification of the SO_2 containing gases.
- (d) Conversion of SO_2 to sulphuric acid.
- (e) Conversion of kiln clinker to cement.

The raw materials used are:-

- (1) Gypsum;
- (2) A source of carbon, e.g. coke;
- (3) A source of silica, e.g. sand or clay;
- (4) A source of alumina, e.g. clay or ash;
- (5) A source of ferric oxide, e.g. ash, pyrites, cinders or mill scale.

The various steps of the process involved are

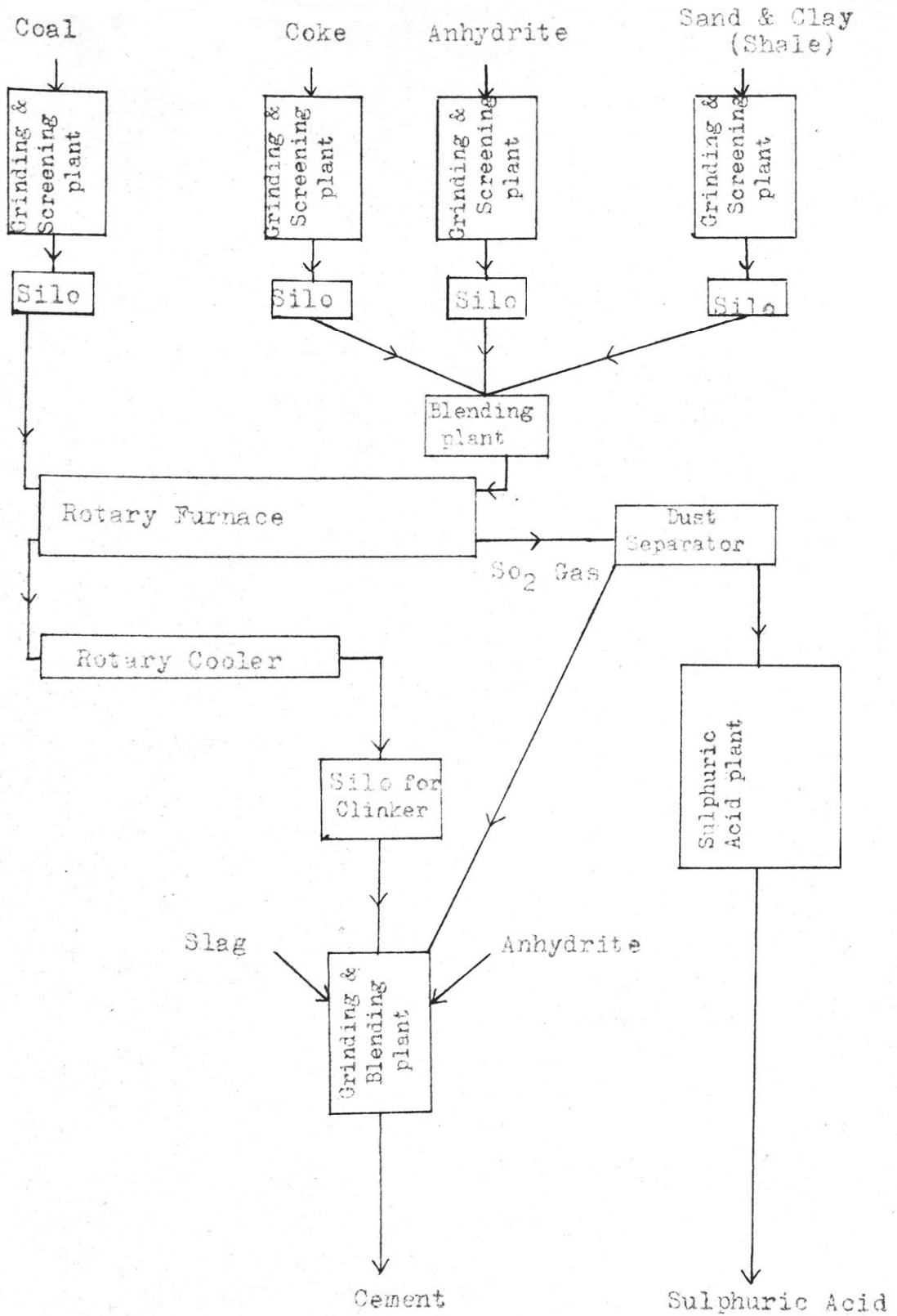


Fig. 9.1.1

shown in the flow sheet.

(a) Production and Preparation of Raw Material:-

The gypsum seam is drilled and blasted in the usual way. Diesel trucks are used for moving the material to avoid laying of track required for tubs. A scraper-loader can be used for loading. The gypsum of two size ranges, 6 inches to $2\frac{1}{2}$ inches and minus $2\frac{1}{2}$ " is brought to the factory site by rail in $25\frac{1}{2}$ ton capacity, bottom opening rail waggons. The waggons are discharged in an intake house at a maximum rate of 200 tons/hour to an underground hopper, from which the material is automatically discharged to a skip hoist which lifts the material 70 feet to a receiving hopper. The receiving hopper is equipped with a tray type jigging feeder which delivers at predetermined rates to a 30 inch belt conveyor, 270 feet long, for transfer to a crushing plant.

A reserve stock pile of 12000 tons capacity can be formed between the waggon unloading station and the crushing plant by means of a friction driven throw off carriage arranged to travel on the conveyor framework for discharge of the material from the belt to ground. Stacking of the material in dumps is accomplished by means of an N.C.K. $\frac{3}{4}$ cu. yd. shovel excavator.

The $+ 2\frac{1}{2}$ inches material can be stocked in the open and the $- 2\frac{1}{2}$ inches material is dumped in a covered store. Material is recovered from the dump areas by means of the excavator, which feeds a travelling hopper,

which is also arranged to travel on the conveyor framework. The travelling hopper has a tray feeder driven by a 5-h.p. oil engine and a two-speed control to deliver the reclaimed gypsum on to the conveyor belt for delivery to the crushing plant. The gypsum flows from the conveyor through magnetic separators to two 3-foot size cone crushers. The crushed material from these machines is transferred by chain and bucket elevators of 120 foot centres to the gypsum storage bunkers.

Sand, Shale and Coke:--

Coke and sand are fed into a common hopper either directly from lorries or from nearby dumps by means of a mobile loader. The shale is fed into a second hopper by lorry, after which it passes through a tray feeder and a magnetic separator on its way to a swing-hammer crusher to reduce it from a feed size which will pass through a 12-inches square mesh grid to a product $1\frac{1}{2}$ inches or less in size. A chain and bucket elevator raises the shale 33 feet to the common hopper for coke and sand, but at no time are materials mixed in this hopper.

The wet coke, sand and shale storage bunkers are loaded with their respective materials from the common hopper by a fully automatic angle type skip hoist, equipped with air operated tripping gear for discharging the skip over the appropriate bunker.

Discharge from the bunkers is controlled at pre-

determined rates by table feeders, which deliver the materials to a rotary drier installation for removal of excess moisture.

The dried materials are delivered from the driers through rotary feeders to a tipping gravity bucket conveyor-elevator, which conveys and elevates the materials simultaneously in alternate buckets to the dried materials storage bunkers.

The storage bunkers feed two 30 inches wide conveyor belts through automatically controlled weighing machines, which are set to trip simultaneously. It is essential to proportion the materials accurately at this stage, and the automatic pre-set weighing machines are controlled from an electrically operated panel equipped with alarm, interlock and trip-out systems.

The correctly proportioned mixture of all four dry materials is discharged from the belt conveyors to two 30 foot long and 8 foot diameter combination tube ball mills in which the materials are ground and mixed. Each ball mill is driven through a turbine gears reduction unit by a 700 h.p. motor. The resultant mixture, known as raw meal, is transported by belt and bucket elevators and Fluidor conveyors to a number of raw meal storage and blending silos. These silos and an adjacent dust bunker are aerated to facilitate emptying.

Raw meal is extracted from the silos at predetermined rates through rotary dischargers equipped with

3-speed change-pole motors, and is delivered to a system comprising belt and bucket elevators and Fluidor conveyors for discharge to kiln feed bunkers. Any excess of raw meal delivered to the kiln feed bunker is returned to the storage silos by means of a Fluidor conveyor system. A Fluidor conveyor is box-shaped in section. The lower half of the section is made into a shallow closed trough by a porous medium on which rests the material to be conveyed. Compressed air is introduced into the trough from below, and this aerates the material, so that it can flow along a slope of as little as five or six percent of the conveyor length.

(b) Production of SO_2 Gas and Clinker:-

Discharge from the feed bunkers is controlled by rotary dischargers for delivery to two rotary kilns each 355 feet long, in which the solid temperatures is raised to about 1400°C . Each kiln is carried on six sets of bearings, and is driven through a Vulcan-Sinclair fluid coupling by a 150 h.p. motor, and is lined with refractory bricks. The kilns are fired with pulverised coal through a 30 foot long firing pipe. Oil is used for starting up.

Coal handling:-

Coal for firing the kilns is delivered to the plant in end-tipping lorries and discharged into a receiving hopper. A jiggling tray feeder delivers the coal at a controlled rate per hour to a chain and bucket elevator

57 feet in height, which in turn delivers through an electro-magnetic separator onto a 20 inches wide belt approximately 100 feet long. The belt passes the coal over a continuous weigher before delivery by means of a friction-driven throw-off carriage to a storage bunker adjoining the kiln firing house. The coal passes to attritors, in which it is pulverised and then fed to the kiln firing pipe together with hot gases supplied by special fans.

Clinker handling:-

The hot clinker from each kiln passes through 12 recuperator tubes, which are outside the kiln and which act as heat exchangers by cooling the clinker and heating the incoming combustion air. The clinker then passes via bifurcated chutes and sieving tray conveyors to jaw crushers to reduce the size to less than $1\frac{1}{2}$ inches.

The crushed clinker is elevated by chain and bucket elevators 80 feet in height to automatic weighers. From the weighers the crushed clinker is transferred to storage bunkers by two 20 inches wide conveyors, each 100 foot long, equipped with heat resisting belts and friction-driven throw-off carriages.

Electric vibrating feeders extract the clinker from these bunkers and deliver it to a system of belt-conveyors and chain and bucket elevators, which convey the material to a 10,000 ton capacity clinker store.

In the apex of the building is a belt conveyor which distributes the clinker by means of a friction-driven throw off carriage to any part of the store, throughout its entire length of 300 feet. Alternatively, the conveyor can deliver to automatically controlled weighing machines, these discharge directly to a belt conveyor which transfers the material to the cement section.

Clinker is reclaimed from the store by bulldozers and loading shovels, which discharge into an underground hopper in the centre of the store. This hopper has a jiggling tray feeder which discharges the material at a controlled rate to a chain and bucket elevator 50 feet high. The material is then delivered to the weigher machines for subsequent transfer to the cement factory.

Equipment and loading arrangements are installed for the disposal of half burnt clinker produced when the kiln is coming on line.

(c) Purification of SO_2 and the Dust Removing Plant:-

The gases leaving the kiln contain about 9% SO_2 , with an appreciable amount of dust which is separated in a smoke box and cyclone. From these units the dust is discharged through rotary seals to a system of tubular vibro conveyors, which deliver to a rotary pulveriser with discharge to a chain and bucket elevator for transfer to the dust bunker by a Fluidor conveyor. The gases are cooled in wash towers which remove the greater part

of residual dust. SO_2 dissolved by water is air stripped and returned to the main gas stream. The dust is finally removed by electrostatic precipitators and the water in the gas scrubbed with counter-current flow of sulphuric acid.

The hot, dusty, moist air from each rotary drier is cleaned before discharge to atmosphere by means of a cyclone separator and wet arrestor. The dust is discharged from cyclones through a rotary seal, for delivery into the main stream of sand, shale or coke.

The dried materials bunkers containing coke and shale and the bunkers containing gypsum are fitted with fully automatic dust filtering plant to exhaust the bunkers during filling: this plant also exhausts the weighers under the bunkers and the conveyor feed shoes during plant operation. Clean air is discharged to atmosphere through an exhaust fan, and the dust is returned to its appropriate bunker through rotary seals.

At the grinding mills the rock is exhausted by scalping cyclones equipped with steam heaters. The cleaned air is discharged to atmosphere through exhaust fans, and the dust is returned to the main stream of material through rotary seals.

A dust-filter plant can be provided which is capable of exhausting dust-laden air simultaneously from all the Fluidor conveyors, belt and bucket elevators

handling raw meal to and from the silos, the raw meal silos and the dust bunker during aeration and filling. The clean air passes to atmosphere and the dust is delivered to the dust bunker through rotary seals from the filter plant, which is located immediately above the bunker.

Two compressors aerate the material in the raw meal silos and the dust bunker. Ancilliary equipment provided with each compressor includes an after cooler, water separator, air-inlet filter and two silencers.

(d) Conversion of SO_2 to Sulphuric Acid:-

SO_2 leaving the drying tower is 6.5% in strength due to the introduction of air to give sufficient oxygen for conversion to SO_3 . The gases pass through blowers and heat exchangers to converters containing a platinum or vanadium catalyst. They are heated to 400°C in the heat exchangers, by gases from the converters.

The reaction being exothermic, temperature is kept low provided the catalyst remains active and a reasonable reaction velocity is assured. Conversion is carried out in stages, removing the interstage heat in the heat exchangers. SO_3 is absorbed after the final stage in 98% H_2SO_4 , which is broken down with weak acid from the drying tower to give 96% H_2O_4 . SO_2 contained in tail gases is removed by scrubbing in water or ammonia liquor to give a solution of ammonium sulphite or bisulphite.

By careful regulation of the pH of the circulating liquor, the loss of NH_3 is kept to the minimum and the SO_2 in the exit gases, expressed as equivalent H_2SO_4 , can be reduced to about 2/3 of a grain/cubic foot. SO_2 obtained by decomposing ammonium sulphite-bisulphite mixture with H_2SO_4 , is returned to the system and the solution containing $(\text{NH}_4)_2\text{SO}_4$ is crystallised to obtain this valuable by-product.

(e) Conversion of kiln clinker to cement:-

For the satisfactory production of cement, good clinker can be produced provided kiln operation and the composition of the raw meal are carefully controlled. The atmosphere in the kiln should be oxidising using 1 : 10 oxygen-air mixture. The ash content of the coal used for firing should be kept in consideration. The clinker is ground with gypsum, stored in silos and packed as required. Every ton of H_2SO_4 produces approximately 1.3 tons of cement.

III. Requirements of the Raw Material and Cost Considerations:-

The raw materials and service requirements are shown in Table 2.3.1. The amounts of basic constituents being calculated according to the ratios, 3 Gypsum: 1 silica: 2 coke: 0.1567 Al_2O_3 : 0.04501 Fe_2O_3 .

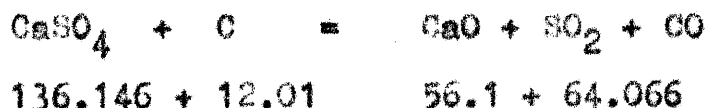
Shale and clay can substitute sand and ash, provided the ratios of silica, alumina and ferric oxide

are kept correctly. For each ton of sulphuric acid 1.76 tons gypsum will be required. To save transport expenditure, the factory should be located, at the site of the raw materials, though the ideal site is rarely available.

Table 9.3.1

Raw Material or Service	Required per ton 100% H_2SO_4	
Gypsum	1.76	tons
Coke	0.082	"
Coal	0.44	"
Sand	0.205	"
Alumina	0.000534	"
Iron oxide	0.00153	"
Electric power	130 k.Wh	
Cooling water	55 m^3	
Fuel (gas or oil)	90 tonne cal.	

For the purpose of arriving at an idea of the amount of cement obtained, the following reaction is to be kept in view:-



As CO burns in oxidising atmosphere to form CO_2 and coke and coal leave little ash it is safe to assume that the weight of cement obtained will correspond to the

combined weight of CaO formed plus the weight of silica and metallic oxides added. As the weight of CaO formed from 1.76 tons of gypsum is 0.573 tons, therefore for each ton of sulphuric acid 1.3 tons of cement will be produced as against 0.92 tons at the Billingham plant.

The amount of coal used to fire the kilns is approximately 25% of the weight of gypsum used. This does not include the fuel required for drying the raw material and initial heating of the kilns.

Capital Costs:-

The actual cost depends on site, availability of services and many other factors. The capital costs of the gypsum mine and of cement plant have been excluded. The minimum economic capacity of plant in U.K. is at least 50,000 tons H_2SO_4 per annum. The ratio of the capital cost of anhydrite - sulphuric acid - and pyrites sulphuric acid plants is about 1.5 to 1.

W. L. Bedwell, (22) gives the following figures for capital and production costs for anhydrite-sulphuric acid plant.

Table 9.3.2
 Capital Cost for Anhydrite-Sulphuric Acid Plant.
 (Output: 150,000 tons H_2SO_4 per annum)

	£
Kiln plant and raw materials preparation	1,500,000
Acid plant	1,300,000
Site development	350,000
Services, acid and anhydrite storage loading, handling and transportation	300,000
Working capital	350,000
Total	£ 3,800,000
£/ton year H_2SO_4	£25 - 30

Table 9.3.3
Production Costs per ton 100 per cent H_2SO_4

	Calcium sulphate contact	Brimstone contact	Pyrites contact
Raw materials	2.00	6.03	5.23
Conversion, including fuel etc.	3.50	0.77	1.65
Overheads, interest and depreciation	3.30	1.00	2.07
	8.80	7.80	8.95
Less credits	1.67	0.30	0.30
Net cost	7.13	7.50	8.65
Size of plant - tons 100% acid per year	60-70,000	60-70,000	60-70,000
Capital cost, £/ton year	28	8.5	17.5

The net cost of H_2SO_4 made in a pyrites-tower plant is £0.5 - £0.75 per ton less than the cost on a pyrites-contact plant and the capital cost is about £14 per ton year H_2SO_4 . A tower plant produced only 77% H_2SO_4 .

The above figures show that though the capital cost is higher, the net cost of sulphuric acid made from gypsum can be lower than that manufactured from pyrites or sulfur, and can be cheaper in Pakistan, where pyrites or good sulfur are hard to get.

CHAPTER X

DISCUSSION and CONCLUSIONS.

The main objective of this work was a study of the rates and mechanisms of the reactions which take place at elevated temperatures in the mixtures used for the manufacture of sulphuric acid and portland cement from gypsum. The author was also interested in the possibility of setting up a plant in Pakistan for the commercial application of this process, and, hence, after establishing the technique using pure laboratory chemicals, the raw materials from Pakistan sources were also included in the systems studied, so that complicating factors, if any, due to differences in purity, crystal structure or general activity could be investigated.

As set out in the previous pages, exploratory work, on the general conditions of reaction and the products formed was first necessary. The system used in commerce is complex, and the conditions of firing in a rotary kiln cannot be duplicated on a small scale in a model kiln, because of the difference in scale, leading to very different heat losses,

temperature gradients and flow conditions. It was essential to establish conditions which produced a product similar to the cement clinker of commerce. By studying the component reactions, under the same conditions, the relative importance of each was to be determined.

BASIC COMPONENTS OF THE MAIN REACTION

Calcium sulphate dihydrate, silica and carbon were used as basic components along with small quantities of Al_2O_3 and Fe_2O_3 . Three moles of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, were used with one mole of SiO_2 and two moles of carbon. Experiments conducted with one mole of carbon or coke produced melts, which are to be avoided in a cement kiln. The best temperature for carrying out the reaction proved to be 1400°C . The ratio of Air to O_2 was maintained at 10:1 throughout, for the production of oxidising atmospheres. Any fluctuation in the amount of O_2 affected the amount of CaS inversely.

BEHAVIOUR OF PAKISTAN RAW MATERIALS

Geological data on the gypsum and coal from Pakistan

is given in Appendix II.

These materials proved to be free from undesirable features. The gypsum was of high purity and showed no significant difference in behaviour from that of pure calcium sulphate dihydrate and hence was substituted in its place during the study of reaction mechanisms.

The coal, although high in sulphur content, was an effective reducing agent. The coke formed from Pakistan coal produced a higher rate of desulphurisation than carbon, due to its more reactive surface and small amounts of catalytic impurities present.

The coal proved to be somewhat less reactive than the coke, while the transient concentration of calcium sulphide was higher due to the higher proportion of volatiles.

The practical conclusion can thus be drawn that the production of sulphuric acid and cement from Pakistan materials is feasible and would not introduce complexities due to the chemical characteristics of the raw materials. The high purity of Pakistan gypsum

results in the production of a stable tricalcium silicate in the final clinker, and does not give lower silicates, due to the absence of free MgO .

OVERALL CHARACTERISTICS OF THE REACTION.

The reaction mixture used commercially for the manufacture of cement and sulphur dioxide consists essentially of anhydrite, coal or coke, silica and small amounts of alumina and iron oxide.

The curves showing the progressive liberation of sulphur dioxide, as a function of time, from similar mixtures are given in Figs. 8.1.1 to 8.1.10. The curve is characterised by a steep initial portion, then a marked turning point to a nearly straight line section of low slope. In an oxidising atmosphere, the reducing agent in the mixture is removed both by reaction with calcium sulphate and reaction with the oxygen. It seemed probable that the turning point in this curve was due to the reducing agent having been consumed. The latter portion of the curve would then represent thermal decomposition of gypsum and reaction with acidic oxides.

In order to confirm this possibility, some of the reaction mixture was taken, after reaction had occurred to a stage beyond the turning point in the curve, reground with carbon and reheated.

The result is shown in Fig. 8.1.10 indicating conclusively that the addition of more carbon greatly speeded up the reaction again and that the turning point in the curve is in fact due to exhaustion of the reducing agent.

The overall curve can thus be considered as made up of two distinct sections, one indicating the rate of reaction in the presence of reducing agent, the second representing the rate of reaction in the absence of reducing agent. Of these, the first section may be considered the more important as the rate of production of sulphur dioxide is much more rapid under these conditions and it accounts for over 80% of the reaction. Without a reducing agent, reaction would be too slow for industrial purposes at these temperatures.

CONTRIBUTING REACTIONS.

To evaluate the relative importance of the various possible reactions which might make up the overall process, a series of simpler systems were studied. The results of these runs are set out in Chapter VIII, and those which give the most significant information will be discussed below:

1. Thermal Decomposition of Gypsum:

The thermal decomposition of pellets of gypsum alone was examined using pellets of different sizes, one series being twice the weight of the other. It was found that after any period of heating, the amount of decomposition was the same in each pellet, i.e. the percentage decomposition in the larger pellet was half that in the smaller one.

This indicated that the rate of decomposition of gypsum alone was governed by some common factor, independent of the weight of the pellet. This was probably the rate of heat transfer to the tablet. Although the pellets were of different weights, the areas of their lower surfaces were similar and it was through this surface that conductive heat trans-

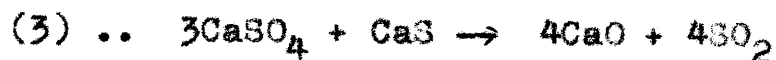
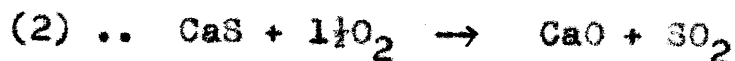
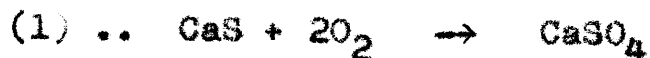
fer would take place. The upper surfaces which would receive most of the radiation were also of similar area.

This result emphasises the point that in reactions between poorly conducting materials, heat transfer may be very important and that the effect of additives which promote the reaction may be to reduce the heat of reaction and thereby make possible more rapid reaction.

The rate of evolution of sulphur dioxide from pure gypsum was compared with that from the mixture corresponding to the composition used commercially in the later stages of reaction after the reducing agent had been exhausted. These did not agree, the rate of evolution from the gypsum pellets being the higher per mass of gypsum present. This is understandable as the heat transfer characteristics would be quite different. In the latter case the pellet is a mixture which, at this stage, would be highly exfoliated.

2. Reaction of Calcium Sulphide in Oxidising Atmospheres:

The most important reactions in which calcium sulphide participate are probably:



When CaS was heated in an oxidising atmosphere at 1400°C , the sulphide sulphur was evolved as SO_2 within ten minutes. No CaSO_4 appeared to be formed in the course of reaction; in fact, whereas the CaS used contained 37.4% CaSO_4 initially, the final quantity of CaSO_4 represented only 18.8% on the same basis. It can be concluded that thermal decomposition of the calcium sulphate initially present occurred and that the CaS was decomposed according to reactions 2 and 3.

3. System: 3 Gypsum - 1 silica:

Heating together silica and gypsum produced a reaction in which the less volatile silica replaced the volatile sulphur trioxide. At these temperatures, sulphur trioxide is broken down into sulphur dioxide and oxygen. The reaction was slower, and the curve (Fig. 8.1.6.) turned at a lower conversion than when

a reducing agent was present as well.

The reaction proceeds relatively rapidly, and at constant rate, to about 37% desulphurization after which the rate falls off sharply.

Since a ratio of 3 gypsum : 1 silica was used, it appears that the reaction to monocalcium silicate is the most rapid while further reaction to di- or tri- calcium silicate is considerably slower.

4. Systems : Gypsum - carbon
Gypsum - coke
Gypsum - coal

The reactions between gypsum and various reducing agents (carbon, coke and coal) were examined in oxidising atmospheres and in nitrogen at temperatures of 1100 and 1400°C. The resulting sulphide concentrations and the evolution of sulphur dioxide as a function of time are shown in Figs. 8.1.7.; 8.3.23 - 25.

The rate of evolution of sulphur dioxide is considerably higher at 1400°C than at 1100°C. Considered in conjunction with the figures for CaS concentration, it is apparent that the increase in temperature

has its greatest effect on the secondary reaction between CaS and CaSO_4 . This is in accordance with the thermodynamic results. Whereas, at 1100°C the sulphide concentration reaches a maximum of 13% at between five and ten minutes, at 1400°C , the maximum occurs before one minute and the concentration falls, from about 10% continuously after that time.

Coke was the most active of these three reducing agents from the point of view of producing desulphurization. (Fig. 8.1.7.)

The use of coal produced a higher intermediate concentration of calcium sulphide due to its high content of volatile reducing matter. The use of coal had the disadvantage of producing a fog of tarry material in the furnace.

The presence of iron or aluminium oxide had the effect of slightly increasing the intermediate concentration of sulphide at 1100°C , but of slightly decreasing it at 1400°C .

A very rapid initial evolution of sulphur dioxide resulted from the previous dehydration of the gypsum. Seventy-three per cent of the sulphur appeared as sulphur dioxide within the first minute.

Activation Energy for Reduction of Calcium Sulphate by Coke.

The early part of these curves approximates closely to a straight line indicating a constant overall rate of reaction. Both the reduction of the calcium sulphate and subsequent reaction play a part in the changes. The rate of heat transfer will also be a factor but the temperature coefficient of the change of rate seems greater than can be accounted for as a result of heat transfer alone. It is of interest to calculate an overall activation energy for the early stage of the reaction. This cannot be taken as a true activation energy which is associated with a particular reaction.

From Run XVII

Slope of curve at 1100°C = 4.6 per cent desulphurization per minute.

Slope of curve at 1400°C = 40 per cent per minute.

Applying Arrhenius' equation:

$$\therefore \ln \frac{k_1}{k_2} = \frac{\Delta E}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right) = \frac{\Delta E}{1.98} \left(\frac{300}{(1400 \times 1100)} \right)$$

$$2.303 \log. \left(\frac{40}{4.6} \right) = \frac{\Delta E}{1.98} \left(\frac{300}{(1400 \times 1100)} \right)$$

$$\begin{aligned}
 \Delta E &= 2.303 \log. \left(\frac{40}{4.6} \right) \times \frac{1.98}{300} \times 1400 \times 1100 \\
 &= 2.303 \times \frac{0.9393 \times 1.98 \times 1400 \times 1100}{300} \\
 &= 21,990 \text{ calories.}
 \end{aligned}$$

This fairly high "activation energy" is absorbed mainly by the reaction between CaS and CaSO_4 .

The addition of small quantities of iron and aluminium oxides made no significant difference in the activation energy of this group of reactions.

The use of dehydrated gypsum considerably increased the rate of reaction at both temperatures due partly to the fact that no water had to be removed but mainly to the greater activity of the freshly dehydrated crystal lattice. This is in accordance with observations that the activity of dehydrated gypsum is greater than that of anhydrite.

The activation energy for reduction of dehydrated gypsum was calculated similarly :

$$\text{Rate at } 1100^\circ\text{C} = \frac{49}{5} = 9.8\%/\text{min.}$$

$$1400^\circ\text{C} = 73\%/\text{min.}$$

$$\begin{aligned}
 \therefore \Delta E &= 2.303 \log \left(\frac{73}{9.8} \right) \times \frac{1.98}{300} \times 1400 \times 1100 \text{ cal.} \\
 &= 2.303 \times 0.8721 \times \frac{1.98}{300} \times 1400 \times 1100 \\
 &= 20,410 \text{ calories.}
 \end{aligned}$$

Thus, for the reaction using dehydrated gypsum, the reaction rates at 1100 and 1400°C are considerably higher than for gypsum but the relative rates and hence the activation energies are similar.

5. The Effect of Additions of Iron and Aluminium Oxides:

In all cases, the desulphurisation produced in the presence of iron oxide was greater than that produced in the presence of aluminium oxide, before the first 5 minutes of the reaction.

In comparing the later stages of reaction, two cases may be distinguished. When the proportion of the reagents is such that calcium sulphide is produced or is initially present in the ratio of $3\text{CaSO}_4 : \text{CaS}$, there is no significant difference between the degree of desulphurisation produced by the two additives. This is apparently due to the rapid and complete reaction between CaS and CaSO_4

in these proportions.

When the ratio of CaSO_4 : CaS is less than 3 : 1 (e.g. system XXVII), the greater catalytic activity of iron oxide, in decomposing the excess calcium sulphate, leads to greater desulphurisation throughout the course of reaction as compared to alumina in System XXVI. (Fig. 8.3.33).

6. Systems : Gypsum - silica - carbon
Gypsum - silica - coke
Gypsum - silica - coal

A comparison of the three reducing agents in these systems shows, that coke is most effective in producing desulphurisation in the overall reaction under the conditions of these experiments. Sugar carbon showed a slight advantage in the initial stages, while coal produced the greatest intermediate concentration of calcium sulphide.

The activity of coke may be attributed to its active surface and the presence of catalytic impurities such as iron oxide. The finely divided structure of the sugar carbon gives it greater activity at low temperatures. The expulsion of volatile matter from the coal and coke will be an endothermic process,

which may cause a lag in temperature rise of the mixture initially.

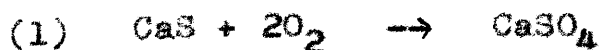
7. Formation and Removal of Calcium Sulphide.

Some of the most important mechanisms which contribute to the changes in this system, are those involving the intermediate formation of calcium sulphide. The concentration of sulphide was measured in all runs and showed the changes typical of an intermediate formed in a series of consecutive reactions. Its concentration changes are shown in Figs. 8.3.25; 8.3.27 and 8.3.29.

In each case it rises to a maximum and then decays as the second stage of reaction becomes significant; calcium sulphide can be formed by the reduction of calcium sulphate by carbon or carbon monoxide.

It may subsequently be removed by reaction with oxygen (if the atmosphere is oxidising), with calcium sulphate or with sulphur dioxide.

The latter reactions are represented by the equations:





No measurable sulphur was formed in any of the reactions, so reaction (3) was considered to be negligible.

Because of its importance, this series of reactions was studied by several procedures.

The results of heating calcium sulphide in an oxidising atmosphere have already been discussed and it was concluded that no net increase in calcium sulphate occurred. This indicates that reaction (1) is unimportant at 1400°C.

In System XX (Table 8.3.54), gypsum and calcium sulphide were heated together at 1400°C in an atmosphere of nitrogen. The rate of evolution of SO_2 was very rapid at first and began to fall off, when about three quarters of the total sulphur had been evolved. Estimations of the sulphide present at each stage of the reaction established that the sulphide had been completely eliminated in five

minutes. The disappearance of sulphide sulphur from the reaction mixture corresponded closely to the turning point in the curve.

The oxidation of calcium sulphide both by oxygen and by calcium sulphate were rapid reactions, particularly in the initial stages. This accounts for the transient existence of calcium sulphide in the reaction mixture.

When gypsum was heated with a reducing agent in an atmosphere of nitrogen at 1100°C , the sulphide concentration rose to 13% by weight at 5 to 10 minutes and again fell off in the typical fashion (Figs. 8.3.25 ; 8.3.27 and 8.3.29). At 1400°C , the rate of the reaction between calcium sulphide and calcium sulphate becomes much higher, relative to the rate of formation of calcium sulphide, so that the maximum sulphide concentration occurs earlier. From one minute onwards, a steady fall in sulphide concentration occurs from about 10% by weight.

PROBABLE MECHANISM and RATE CONTROLLING STEP

Based on the foregoing results, a picture can be built up of the probable course of the overall reaction.

The first stage of the reaction, in the case of gypsum would be its dehydration. In the gypsum lattice the sulphate and calcium ions are bonded in planes, held together by hydrogen bonding through water molecules. Upon the removal of water, the bonds between various layers are broken and the crystal becomes in effect, a pile of discrete layers (Figs. 8.3.34 and 8.3.35). The edges of these laminae are points of extremely high activity, at which interaction with other substances could well begin.

The next stage could be ..

- (a) further thermal decomposition of gypsum
- (b) reaction of the dehydrated gypsum with silica
or
- (c) reaction of the gypsum with reducing agent.

While (a) and (b) go on to some extent, the most important reaction at this stage is the reaction with reducing agent. This is shown by the fact that CaS

is formed as an intermediate compound, which appears in the first few minutes of the reaction. Reduction to CaS occurs at temperatures, at which reactions (a) and (b) have been shown to go on only very slowly.

It has never previously been established definitely whether the reduction takes place as a reaction directly between carbon and dehydrated gypsum or whether CO is always the active reducing agent. This point was investigated by heating various forms of carbon with gypsum in an atmosphere of nitrogen both at 1400° and 1100°C . Rapid reaction occurred in these cases without any induction period.

The mechanism of the process was further investigated by packing macro-crystals of gypsum in carbon and heating again in nitrogen. As described previously, a sulphide layer was rapidly formed around the edges of the crystal laminae, as shown by the sulphide prints (Figures 8.3.36; 8.3.37a and 8.3.37b). The sulphide can then be removed by reaction with O_2 (when the atmosphere is oxidising) or with CaSO_4 .

The reaction between CaSO_4 and CaS was favoured by

the presence of silica, and to a lesser extent by Fe_2O_3 as shown in Figures 8.3.31 and 8.3.33.

A noteworthy feature of the results of these studies was the remarkably rapid reaction between gypsum and coke in an atmosphere of N_2 , in which 80% desulphurisation was reached in 5 minutes, without the aid of an oxidising atmosphere, or any additive such as silica. This is interesting as the evolution of SO_2 is the result of at least two consecutive reactions between solids - (a) reduction by coke
and (b) interaction of CaS and CaSO_4 .

A complete study of the diffusional processes involved in these two reactions would be of great interest.

At 1400°C , the desulphurisation process is thus rapid, provided a reducing agent is present. The rate controlling step appears to be the reduction to sulphide, since its concentration rises initially to a low value, falls off and is essentially zero during most of the reaction.

The rate of reaction falls off sharply, when the

reducing agent is exhausted, and the evolution of SO_2 from then on, would be due to thermal decomposition of the remaining sulphate hindered by poor conditions of thermal conductivity and the fact that it is now being incorporated in a clinker or melt.

CEMENT CLINKER

The quenching method proved successful for getting large crystals of the clinker components, especially tricalcium silicate, which is a constituent of prime importance in the clinker. These crystals are shown in the photographs taken by the Vickers Microscope. Due to the large size of the crystals, the magnification employed was X194, as compared to the usual X500. Their examination was done by petrographic methods, which showed the presence of two crystalline phases, in addition to glass. The phase composition was as follows:--

- (1) Tricalcium silicate 90%
- (2) Brownmillerite 6 - 8%
(tetracalcium aluminoferrite C_4AF)
- (3) Glass 2 - 4%

This shows that the clinker obtained from System XIII

has a much higher tricalcium silicate content, as compared to general clinkers, which normally do not contain above 45 - 53%. The production of a good cement clinker has thus been realised. The glass content, as desirable, is fairly low.

Brownmillerite is a dibasic compound and is formed in place of the tribasic C_3A , which process releases CaO . This CaO then is available for combination with C_2S to form C_3S . In the final product no free CaO or MgO was found. Free CaO affects the burnability of cement adversely and MgO increases the C_2S at equilibrium.

A description and cost considerations of the proposed plant for the manufacture of sulphuric acid and cement have been given in Chapter IX. By employing the composition of System XIII 1.3 tons of cement per ton of sulphuric acid produced, can be obtained.

SUGGESTIONS FOR FURTHER WORK.

The following appear to be the lines which could be useful for further work:

1. Additional studies of the nucleation and diffusional mechanisms in the solid state reactions involved, such as the reaction between gypsum and carbon, gypsum and silica and calcium sulphate and calcium sulphide. A comparison of the behaviour of an anhydrite lattice and a freshly dehydrated gypsum lattice would be of value.
2. Steam has been reported to have a marked catalytic effect on this set of reactions, and would warrant further investigations.
3. Departing more widely from the present line of approach, an examination of the behaviour of similar systems upon heating in a retort in the absence of air, could be of economic importance.

This process has the advantage of producing a mixture of sulphur and concentrated sulphur dioxide which permits the economic operation of a smaller sulphuric acid plant, although the problem of a sulphide free clinker will have to be tackled with.

BIBLIOGRAPHY.

1. Adadurov, I.E.
J. Appl. Chem. Russia. 5, 157-162 (1932)
Brit. abstr. A.1213 (1932).
2. Adadurov, I.E. and Fligunov, V.P.
J. Appl. Chem. Russia. 5, 149-156 (1932)
Brit. abstr. A.1213 (1932).
3. Adadurov, I.E.; Deribas, D.E. and Kraine, P.Y.
J. Appl. Chem. Russia. 3, 509-531 (1930)
Brit. abstr. A.318 (1931).
4. Adadurov, I.E.; Galaneeva, A. and Gernet, D.V.
J. Appl. Chem. Russia. 5, 897-901 (1932)
Chem. abstr. 27, 1566 (1933).
5. Ahernan, R.
Przem. Chem. 8, 314-317 (1952)
Brit. abstr. B1. 139 (1953).
6. Anderson, J.S. and Merton, M.C.
Proc. Royal Soc. London. A184, 83 (1945).
7. Anon:
Fr. 375, 469, March 8, 1907.
Chem. abstr. 2, 2607 (1908).
8. Ausies, J.
Fr. 420, 675, Sept. 20, 1910.
Chem. abstr. 6, 1968 (1912).

9. Badische Anilin and Soda Fabrik.
 Ger. 305, 123, Oct. 30, 1919.
 Chem. abstr. 17, 3578 (1923).
10. Badische Anilin and Soda Fabrik.
 Ger. 301, 682, 1919.
 Chem. abstr. 17, 3578 (1923).
11. Badische Anilin and Soda Fabrik.
 Ger. 302, 433, Dec. 24, 1919.
 Chem. abstr. 17, 3578 (1923).
12. Badische Anilin and Soda Fabrik.
 Ger. 306, 312, Feb. 17, 1920.
 Chem. abstr. 17, 3578 (1923).
13. Badische Anilin and Soda Fabrik.
 Ger. 302, 471, Feb. 17, 1920.
 Chem. abstr. 17, 3578 (1923).
14. Bamback, A.
 Ital. 139, 955, Feb. 24, 1914.
 Chem. abstr. 9, 2804 (1915).
15. Bamback, A.
 Brit. 3, 174, Feb. 6, 1914.
 Chem. abstr. 10, 95 (1916).
16. Bamback and Co.
 U.P. 371, 978, April 16, 1918.
 Brit. abstr. A.605 (1923).

17. Basset, L.P.
Brit. 12, 027, May 21, 1912.
Chem. abstr. 7, 3653 (1913).
18. Basset, L.P.
Fr. 457, 511, July 11, 1912.
Chem. abstr. 8, 2793 (1914).
19. Basset, L.P.
Brit. 17, 873, Aug. 5, 1913.
Chem. abstr. 9, 365 (1915).
20. Basset, L.P.
U.S.1, 168, 046, Jan. 11, 1916.
Chem. abstr. 10, 814 (1916).
21. Basset, L.P.
U.S.1, 198, 817, Sept. 19
Chem. abstr. 10, 2977 (1916).
22. Eedwell, W.L.
"The Production of Sulphuric Acid from
Calcium Sulphate".
Royal Inst. Chem. Lectures, Monographs &
Reports, 3, pp21 (1952).
23. Reumont, J.H.; Willaman, J.J. and De Long, W.A.
Plant. Physiol, 2, 487-95 (1927).
24. Birnbaum and Wittich.
Ber. 13, 651, 1880.
Chem. abstr. 23, 4400 (1929).

25. Bischoff, F.V.
Z. Anorg. Chem. 250, 10 - 22 (1942).
26. Bischoff, F.
Radex - Rund - Schau, 8-13 (1949).
Chem. abstr. 43, 8621 (1949).
27. Bogue, R.H.
"The Chemistry of Portland Cement", Chap. 26.
Reinhold Pub. Corp. New York (1955).
28. Bogue, R.H.
"The Chemistry of Portland Cement". pp. 32
Reinhold Pub. Corp. New York (1955).
29. Briner, E.
Helv. Chim. Acta. 28, 50-9 (1945).
30. Briner, E. and Enodel, C.
Helv. Chim. Acta, 27, 1406-1414 (1944).
31. Briner, E.; Pamm, G. and Paillard, H.
Helv. Chim. Acta. 31, 2220-35 (1948).
32. Briner, E.; Pamm, G. and Paillard, H.
Helv. Chim. Acta. 32, 635-646 (1949).
33. Dudnikoff, P.P.
Chem - Ztg. 49, 430-431 (1925).
Brit. abstr. B.543 (1925).

34. Budnikoff, P.P. and Syrkin, J.K.
Chem. Zeit. 4722 (1923)
Brit. abstr. A11. 72 (1923).
35. Budnikov, P.P. and Nekrich, M.I.
J. Applied Chem. U.S.S.R. 5, 173-6 (1932)
Chem. abstr. 26, 4930 (1932).
36. Budnikoff, P.O. and Rivolin, I.I.
J. Appl. Chem. Russ. 11, 1129-1150 (1938)
Brit. abstr. B.478 (1939).
37. Budnikov, P.P.; Shicharevitsch & Lukova, S.D.
J. Chem. Ind. Russ, 10, No.8, 36-40(1934)
Brit. abstr. B.23 (1935).
38. Caddick, A.J.
Chem. Trade J. 86, 569-570 (1930).
39. Cathala, J.
Proc. Intern. Congr. Pure & Appl. Chem.
(London) 11, 35 - 48 (1947)
Chem. abstr. 44, 5229 (1950).
40. Cathala, J.
Compt. rend. 78e. Congr. soc. Savantes.
Paris et depts. Sect. sci. 471 - 475 (1953).
41. Charmandarian, M.S. and Martschenko, G.V.
J. Chem. Ind. Russ. 10, No. 4, 42-44 (1934)
Chem. abstr. 28, 4841 (1934)

42. Charrin, V. Rev.
Materiaux Construction trav. publics. c.
373, 86 - 88 (1946)
Chem. abstr. 41, 6377 (1947).
43. Chevalier - Girard.
Fr. 660, 916, Jan. 5, 1928.
Chem. abstr. 24, 209 (1930).
44. Dominik, W.
Przenysl. Chem. 5, 185-91 (1921)
Chem. abstr. 17, 1692 (1923).
45. Dowden, D.A. and Garner, W.E.
J. Chem. Soc. 894, (1939).
46. Edgcombe, L.J. and Crossley, H.E.
"Improved Methods for Quantitative
Analysis of Coal-ash and Coke-ash".
Fuel Research Survey paper No. 50.
Dept. of Scientific & Industrial Research
Britain (1949).
47. Edwards, W.A.M.
Chem. & Ind. 764-73 (1952).
48. Farbenind, I.G.
A-G. Fr. 658, 727, 8th Aug. 1928.
Chem. abstr. 23, 5279 (1929).

49. Fischbeck & Snaidt.
Z. Electrochem. 38, 199 (1932).
50. Fleck, A.
Chem. & Ind. 1184, Dec. 6 (1952).
51. Fleck, A. and I.C.I. Ltd.
B.P. 328, 128, 9th May, 1929.
Brit. abstr. B. 862 (1930).
52. Franklin, R.G. and Pace, G.H.
Brit. 719, 235, Dec. 1, 1954.
Chem. abstr. 49, 7821 (1955).
53. Frey, H.
Z. Angew. Chem. 22, 2375-7 (1910)
Chem. abstr. 4, 648 (1910).
54. Frydlender, J.H.
Rev. prod. chim. 29, 613-6, 649-54 (1926)
Chem. abstr. 21, 476 (1927).
55. Fujü, K.
Govt. Chem. Ind. Research Inst. Tokyo:
"Gypsum". 1, 320-3 (1952)
Chem. abstr. 47, 4778 (1953).
56. Garner, W.E.
J. Chem. Soc. 1239 (1947).
57. Garner, W.E. and Kingman, F.E.T.
Trans. Fara. Soc. 27, 232 (1931).

58. Garner, W.E. and Veal, F.J.
J. Chem. Soc. 1436, 1487 (1935).
59. Gavanda, L.
Mitt, Chem. Forsch - Inst. Ind. Österr.
3, 70 - 3 (1949)
Chem. abstr. 44, 806 (1950).
60. Harris, G.J. and I.C.I. Ltd.
Brit. 309, 661, Feb. 6, 1928.
Chem. abstr. 24, 706, (1930).
61. Harvey, R.B. and Regeumbal, L.O.
Plant Physiol, 1, 205-6 (1926).
62. Higson, G.I.
Chem. Eng. News, 29, 4469-74 (1951).
63. Hildebrand, W.F.
"Analysis of Silicate and Carbonate Rocks".
Bull. 700, U.S. Geological Survey (1919).
64. Hofman, H.O. and Mostowitsch, W.
Tran. Am. Inst. Min. Eng. 39, 628-653,
(1908).
65. Hofman, H.O. and Mostowitsch, W.
Trans. Am. Inst. Min. Eng. 41, 763-785
(1911).
66. Honus, Otto.
Zement, 23, 415-19 (1934)
Chem. abstr. 28, 7135 (1934).

67. Hutin, A.
Mon. Sci. 13, 254-5 (1923)
Chem. abstr. 18, 884 (1924).
68. Huttig, G.P. and Bischoff, V.
Reichsamt Wirtschaftsausbau. Chem. Ber.
Prüf - N2. 93 (PB 52008), 171-5 (1940)
(Pub. 1941).
Chem. abstr. 41, 5809 (1947).
69. Kanthal.
"Kanthal Handbook" pp. 82.
Aktiebolaget Kanthal Hallstahammar
Sweden (1951).
70. Kaselitz, U.F.
Z. angew. chem. 33, 49-51 (1920)
Chem. abstr. 14, 2056 (1920).
71. Kern, D.Q.
"Process Heat Transfer" pp.18, Fig. 2.9
McGraw Hill Book Co. (1950).
72. Kühne, H.
Chem.- Ing-Tech. 21, 227-29
Brit. abstr. B1, 299 (1950).
73. Kunze and Sotter.
G.P. 408, 223, June 9, 1922.
Brit. abstr. B.450. (1925).

74. Losev, K.I. and Nikitin, S.N.
J. Chem. Ind. Russia, 6, 169-173 (1929)
Brit. abstr. B. 903 (1930).
75. Manuilova, N.S. and Rojak, S.M.
Trans. All union. Sci. Inst. cement. 10,
122 - 128 (1935)
Brit. abstr. B.377 (1938).
76. Manning, J.
Paint Oil Col. J. 120, 1095 (1951).
77. Manning, J.
Fertilizer Soc. Proc. 15 (1951)
Chem. abstr. 56, 5271 (1952).
78. Marchal, G. Mille.
Compt. rend. 177, 1300 - 1302 (1923).
79. Marchal, G. Mille.
Compt. rend. 176, 299-301 (1923)
Chem. abstr. 18, 509 (1924).
80. Marchal, G. Mille.
J. Chim. phys. 23, 38 - 60 (1926)
Brit. abstr. A. 3 - 59 (1926).
81. Marchal, G. Mille.
J. Chim. phys. 22, 325 - 48 (1925)
Chem. abstr. 19, 3201 (1925).

82. Marchal, G. Mille.
Bull. Soc. Chim. 39, 401-8 (1926).
83. Martin, W. McK.
Ind. Eng. Chem. Anal. Ed. 8, 395-96 (1936).
84. Martin, W. McK. and Green, J.R.
Ind. Eng. Chem. Anal. Ed. 5, 114-18 (1933).
85. Marks, G.C.
G. Polysias. A-G. B.P. 326, 612, Jan 23(1929)
Brit. abstr. B. 556 (1930).
86. Metallbank and Metallurgische.
G.P. 390, 998, Sept. 25 (1917)
Brit. abstr. B. 422 (1924).
87. Metallges A - G.
B.P. 423451, Sept. 29 (1933)
Brit. abstr. B. 495 (1935).
88. Meuris, H.
B.P. 324, 199, Oct. 6 (1928)
Chem. abstr. 24, 3340 (1930).
89. Meuris, H.
Belg. 354, 788, Nov. 30 (1928)
Chem. abstr. 23, 4320 (1929).
90. Mirew, D.
Arch. Eisen hüttenw. 12, 429-31(1938-9)
Brit. abstr. B.491 (1939).

91. Milligan, L.H.
Ind. Eng. Chem. 16, 889, (1924).
92. Molitor, H.
Schweiz. Apoth. Ztg. 62, 517-19,
529-34, 544-48 (1924)
Chem. abstr. 19, 2262 (1925).
93. Molitor, H.
Il. notiz. Chim. Ind. 1, 278-80, 312-4
(1926)
Chem. abstr. 21, 476 (1927).
94. Mullan, T.F.
Rock Products 33, 18, 62-3 (1930).
95. Muller, W.J.
Z. angew. Chem. 39, 169-174 (1926).
96. Muller, W.J.
Umschau 30, 28-30 (1926).
97. Muller, W.J. and Clingenstein, H.
G.P. 388, 849, July 22 (1919)
Brit. abstr. B. 379 (1924).
98. Nadachowski, F.
Przemysl Chem. 9, 55-62 (1953)
Chem. abstr. 48, 8508 (1954).

99. Neumann, B.
Z. angew. Chem. 39, 1537-42 (1926).
100. Newman, E.S.
J. Research Natl. Bur. Standards, 27
191-6 (1941).
101. Parrish, P.
Ind. Chemist, 5, 491-3 (1929).
102. Pavlov, K.F.; Lesokhin, I.G. and Traber, D.G.
J. Chem. Ind. U.S.S.R. 15, No. 3, 5-10
(1938)
Chem. abstr. 32, 5587 (1938).
103. Reynolds, D.A. and Holmes, C.R.
"Procedure and apparatus for determining
carbonizing properties of American coals
by the Bureau of Mines - American Gas
Association Method".
U.S. Bureau of Mines, technical paper
no. 685 (1946).
104. Rhenania, Ver.
F.P. 604, 699, Sept. 30 (1925)
Brit. abstr. B. 788 (1926).
105. Roberts and Anderson,
Rev. Pure Applied Chem. Royal Aust. Chem.
Inst. 2, No. 1 (1952).

106. Rojak, S.M.; Gerschman, M; Miloslavski, K.;
and Nagerova, E.
J. Chem. Ind. Russ. 10, No. 7, 35-41 (1933)
Brit. abstr. B. 16, (1934).
107. Rojak, S.M.; Gerschman, M.I.; Miloslavski, K.P.;
and Nagerova, E.
Trans. All. Union. Sci. Inst. Cement, 10,
5 - 21 (1935).
Brit. abstr. B. 377 (1938).
108. Rothe, F. and Brenek, H.
U.S. 1, 790,023, Jan. 27 (1931)
Chem. abstr. 25, 1346 (1931).
109. Schenck, R. and Jordan, K.
Z. anorg. allgem. Chem. 178, 389-99(1929)
110. Schenck, R. and Hammerschmidt, F.
Z. anorg. allgem. chem. 210, 305-12 (1933).
111. Scot and Furman.
"Standard Methods of Chemical Analysis".
p. 214-15.
The Technical Press Ltd. London (1939).
112. Seailles, J.C.
B.P. 643, 479, July 29 (1947)
Brit. abstr. B1. 432 (1951).

113. Sestini.
 Ber. 7, 1295 (1874).
 Chem. abstr. 23, 4400 (1929).
114. Shapiro, L. and Brannock, W.W.
 "Rapid Analysis of Silicate Rocks".
 Geological Survey Circular No. 165
 U.S. Dept. of Interior (1952).
115. Stetser, J.B. and Norton, R.H.
 "Combustion train for Carbon Determination".
 The Iron Age, 102, No. 8, 443-445
 Aug. 22 (1918).
116. Steward, G.E.
 Rev. Quim. industr. B. Aires, 2, No. 15,
 20 - 26 (1942)
 Brit. abstr. B1, 231 (1950).
117. Teraschkevitch, V.R. and Zvetzki, G.N.
 J. Appl. Chem. Russia, 9, 2155-2175 (1936)
 Brit. abstr. B.665 (1937).
118. Terrea, E.
 Z. angew. Chem. 44, 356-363 (1931).
119. Tetens.
 G.P. 380, 621, March 29 (1922)
 Brit. abstr. A.1224 (1923).

120. Trifonov, I.V.
Metall. u. Erz 29, 364-5 (1932)
Chem. abstr. 26, 5885 (1932).
121. Trifonov, I.V.
Metall. u. Erz. 30, 46-7 (1933)
Brit. abstr. B.495 (1935).
122. Tsytovitch, E.V.
Chim. Promychl, 4, 119-24 (1926)
Chimie et industrie 16, 602-3 (1926).
123. Veidenmanis, A.
Latvij. Univ. Raksti, 3, 385-415 (1937)
Brit. abstr. B.665 (1937).
124. Volkovich, S.I.
Min. Suir. 7, No. 11-12, 44-49 (1932)
Brit. abstr. B. 913 (1933).
125. Waeser, B.
Erdol u. Kohle, 5, 497-499 (1952)
Brit. abstr. B1. 139, (1953).
126. Wasilewski, L.; Zaleski, J.Z.; Kaczorowski, A.
and Badzynski, W.
Pszemysl Chem. 18, 633-647 (1934)
Brit. abstr. B. 146 (1935).
127. Weaver, E.R. and Edwards, J.D.
Ind. Eng. Chem. 7, 534-35 (1951).

128. Wedekind, R. and Co.
Ger. 232, 734, Apr. 12 (1910)
Chem. abstr. 5, 2710 (1911).
129. Weeren, F.
Ger. 301, 712, Oct. 25 (1919)
Chem. abstr. 17, 3578 (1923).
130. Weyer, I.
Zement, 20, 714 (1931)
Chem. abstr. 25, 5744 (1931).
131. Wilson, M.
U.S. 2528,103, Oct. 31 (1950)
Chem. abstr. 45, 1320 (1951).
132. Wohler, L.; Martin, P. and Schmidt, E.
Z. anorg. chem. 127, 273-294 (1923).
133. Zawadzki, J.
Z. anorg. allgem. Chem. 205, 180-90(1952).
134. Zawadzki, J. and Syryczynski, Z.
Roczniki. Chem. 10, 715-27; 727-28. French
(1930)
Chem. abstr. 25, 1174 (1931).
135. Zawadzki, J. and Sobieraj, Z.
Przemysl. Chem. 18, 668-76 (1934)
Chem. abstr. 29, 6014 (1935).

136. Zawadzki, J. and Weychert, S.
Przegląd Chem. 5, 245-54 (1947)
Chem. abstr. 43, 2377 (1949).
137. Zawadzki, J.; Kossak, K. and Narbut, H.
Przemysł Chem. 5, 225-36 (1921)
Chem. abstr. 17, 1692 (1923).
138. Zelinskii, N. D. and Rakuzin, M.A.
Compt. rend. acad. sci. U.R.S.S. 471-4
(1930A)
Chem. abstr. 25, 4978 (1931).

ANALYSIS OF COAL and COKE SUPPLIED by P.I.D.C.COMMONWEALTH SCIENTIFIC and INDUSTRIAL
RESEARCH ORGANIZATION.COAL RESEARCH SECTION.

Ref.No. F294/6184/56 ... Coal from Pakistan (container
labelled:
Dry Coal - To P.I.D.C., K1/C
from Mari Indus.
RWC.
MTA 2/24
CANARA

Ref. No. F294/6185/56 ... Char from above coal
Carbonising temperature 800°C
Weight of coal carbonised
= 3930 grammes
Coke Yield = 2340 grammes.

	Coal	Char
<u>Air-dried Basis</u>		
Moisture	3.2	1.1
Ash	18.1	30.2
Volatile matter	41.8	1.5
Fixed carbon	36.9	67.2
Carbon	56.9	-
Hydrogen	4.4	-
Total Sulphur	6.7	6.3
<u>D.A.F. Basis</u>		
Volatile matter	53.2	2.2
Carbon	72.4	-
Hydrogen	5.7	-

A P P E N D I X I I .GEOLOGICAL DATA of COAL and COKE.C o p y .Pakistan Industrial Development Corporation.

Peyedecce House,
 Kutchery Road,
 Karachi. 3.
 (Pakistan).

December 10, 1956.

C&C/Gyp-4(1)/Misc.

The High Commissioner for Pakistan
 in Australia and New Zealand,
 Dalton House,
 115 Pitt Street,
 SYDNEY.

Subject: .. Supply of Mineral Samples for
 Mr. Mohamed Saeed Zahid a
 Colombo Plan Scholar in Australia.

Dear Sir,

Kindly refer to your letter No. 34/CP/53 dated
 12.11.1956, addressed to the Secretary, Pakistan
 Council of Scientific and Industrial Research,
 Karachi, copy of which has been transmitted to us.

We give below the required information in respect
 of Coal and Gypsum:

<u>Mineral</u>	<u>Name of the City</u>	<u>Name of the Mine</u>	<u>Name of the Seam</u>
Coal	Makerwal Distt. Mari- Indus.	Makerwal Collieries P.I.D.C.	Semi-bituminous coal tertiary lower eocen.

<u>Mineral</u>	<u>Name of the City</u>	<u>Name of the Mine</u>	<u>Name of the Seam</u>
Gypsum	Daudkhel Distt. Mianwali	Gypsum Quarry P.I.D.C.	No name. Tertiary deposits upper eocen.

Yours faithfully,

Pakistan Industrial Development Corporation.

(sgd) M.A.BASITH.
Operative Director (Collieries).

Copy forwarded to the Technical Secretary, Pakistan Council of Scientific and Industrial Research, Block No. 95, Pakistan Secretariat, Karachi, with reference to his letter No. 519/136/54 dated 30.11.1956.



>006941737

