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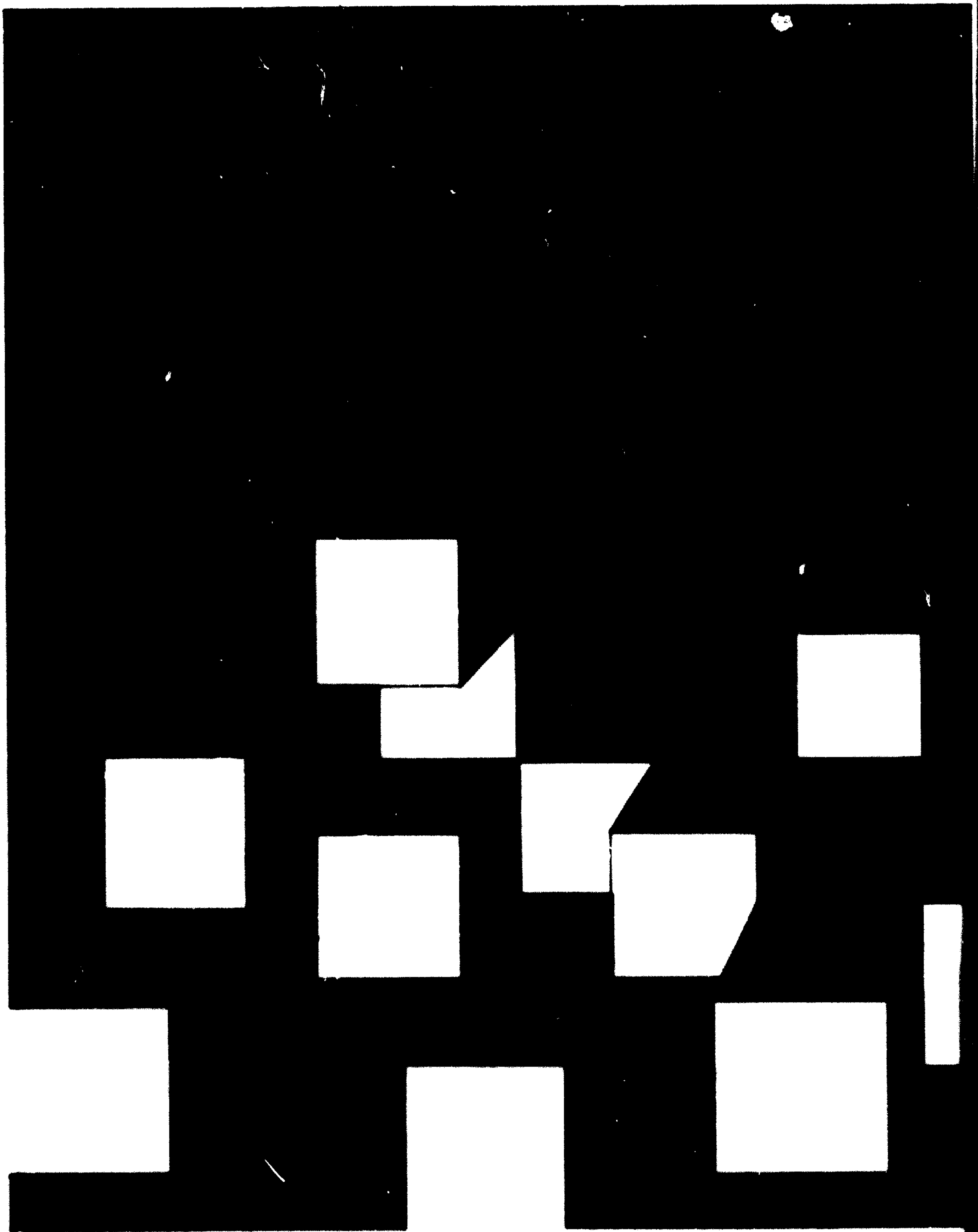

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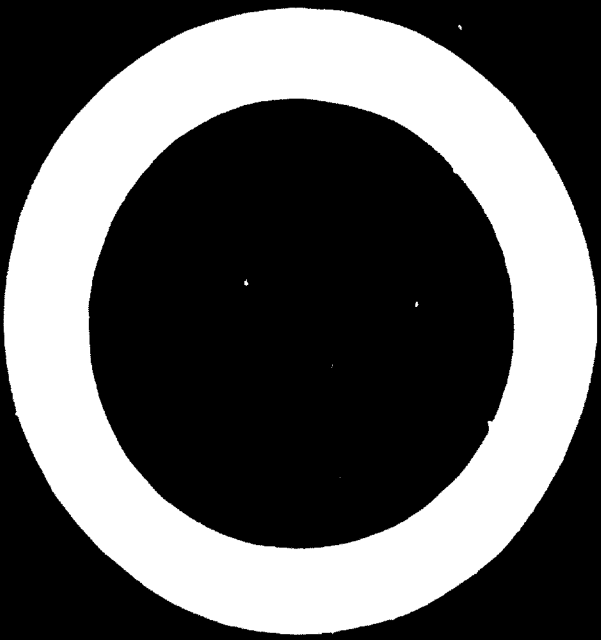
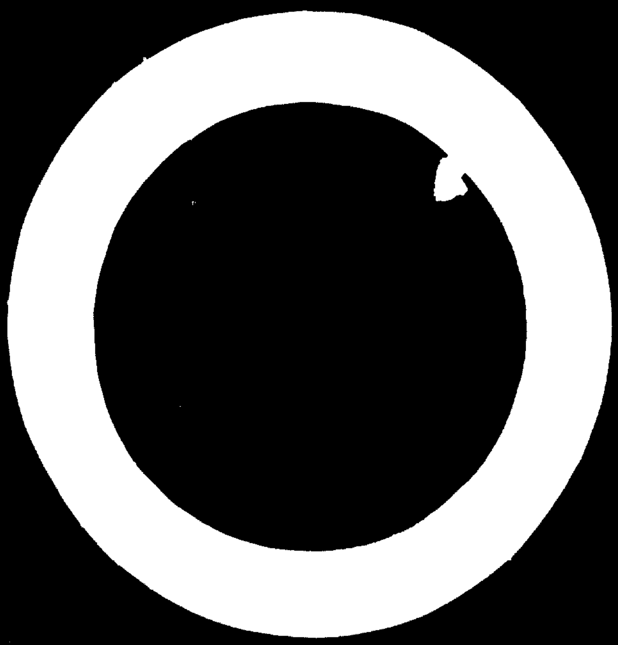


THE MANUFACTURE OF CEMENT AND SULPHURIC ACID FROM CALCIUM SULPHATE



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
VIENNA

THE MANUFACTURE OF CEMENT AND SULPHURIC ACID FROM CALCIUM SULPHATE

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Foreword

The data given in this report will enable a developing country to make an approximate assessment of the costs of making sulphuric acid and cement from sulphur or pyrites and limestone and from the various forms of calcium sulphate. They will also enable the costs of making sulphuric acid from sulphur, pyrites and calcium sulphate to be compared. The cost assessments can only be approximate for an unknown site in an unknown country, but they will enable a developing country to decide the method of making sulphuric acid for which it wishes to obtain accurate cost estimates.

This publication has been prepared by Mr. W. L. Bedwell in the capacity of consultant to UNIDO. The views and opinions expressed in this publication are those of the consultant and do not necessarily reflect the views of the secretariat of UNIDO.

Contents

EXPLANATORY NOTES

Dollar ($) refers to US dollar unless otherwise specified.
£ refers to pound sterling.
References are indicated in parentheses in the text, by name of author and year of publication. The full references are listed alphabetically at the end of the paper.

The following abbreviations are used in this publication:

atm	atmosphere
B.O.V.	brown oil of vitriol
cm	centimetre
cm^2	square centimetre
°K	degree Kelvin
ft	foot
f. o. b.	free on board
g	gram
g cal	gram calorie
g mole	gram molecule
in	inch
kcal	kilogram calorie
kg	kilogram
lb	pound
L.S.F.	lime saturation factor
m	metre
m^2	square metre
R.O.V.	rectified oil of vitriol
ton	long ton (2,240 lb)
tonne	metric ton (1,000 kg)
t cal	tonne calorie

INTRODUCTION

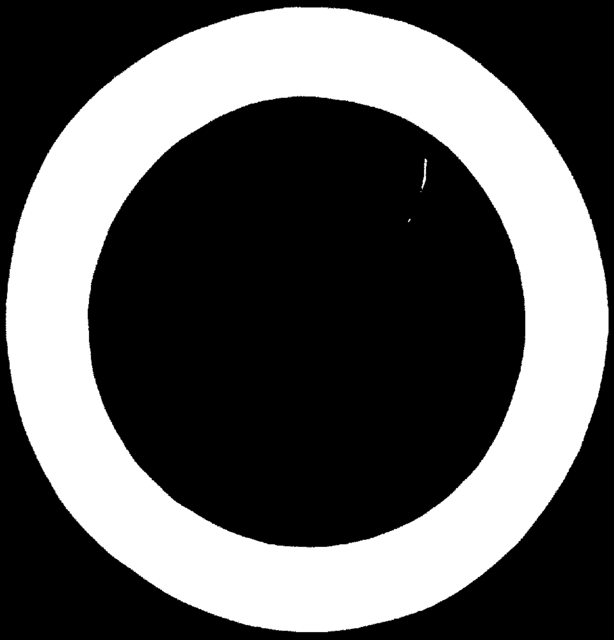
Conventional methods for the manufacture of Portland cement and sulphuric acid are considered first in this paper and then production from calcium sulphate.

The composition and major constituents of Portland cement made from limestone and their hydraulic properties are given in the first chapter, followed by a typical specification for Portland cement. A plant for the production of Portland cement from limestone is described, capital costs are stated, and raw material and other requirements are indicated.

The second chapter describes plants for the preparation of sulphur dioxide from elemental sulphur and pyrites, the oxidation of sulphur dioxide to sulphur trioxide and the production of sulphuric acid from sulphur trioxide. The thermodynamics and kinetics of the oxidation reaction are discussed and capital costs, with raw material and other requirements are given. The availability of elemental sulphur and pyrites is considered.

The replacement of limestone in the manufacture of Portland cement by mineral forms of calcium sulphate is dealt with in chapter three. The chemical reactions that occur when calcium sulphate is used are discussed and a plant to make sulphuric acid and Portland cement from mineral calcium sulphate is described. Capital costs, raw material and other requirements are given.

The problems that arise when mineral calcium sulphate is replaced by gypsum produced as a by-product of phosphoric acid manufacture are indicated in the fourth chapter. The effect of the two major impurities present in by-product gypsum on cement quality is considered. The costs incurred by the use of by-product gypsum are stated and possible consequences on the operation of the phosphoric acid plant on which the gypsum is made are indicated.



1. PORTLAND CEMENT

A. DEFINITION

Most countries have their own specifications for cement. The British Standard specification given below is an illustration of a standard that a producer might be expected to meet.

British Standard specification BS 12: 1958 "Portland Cement (Ordinary and Rapid-Hardening)" defines cement as:

> "... manufactured by intimately mixing together calcareous or other lime-bearing material with, if required, argillaceous and/or other silica, alumina or iron-oxide-bearing materials, burning them at a clinkering temperature and grinding the resulting clinker so as to produce a cement capable of complying with this British Standard.
>
> "No material other than gypsum (or its derivatives), or water, or both, shall be added after burning.
>
> "An amendment published on 5 November 1962 states that 'traces of metallic iron from the grinding process are not to be regarded as an addition.' "

It should be noted that clinkering is the process of heating to produce incomplete fusion in the material heated. Less than one third of the material heated to produce cement clinker becomes fluid.

Gypsum is added as a retarder to control the setting time of the cement.

B. COMPOSITION

A typical range of analyses for ordinary Portland cement is:

	Per cent
CaO	60 —67
Al_2O_3	3 — 8
Fe_2O_3	0.5— 6
SiO_2	17 —25
MgO	0.1— 4
SO_3	1 — 3

Modern Portland cements have CaO contents in the upper part of the bracket.

The compounds present in cement clinker are formed during heating ("burning") by the interaction of CaO, SiO_2, Al_2O_3 and Fe_2O_3 present in the raw material, together with minor components such as MgO and alkali metal oxides. The four major constituents amount to more than 95 per cent of the clinker. The phase relations in binary and ternary combinations of the major constituents have all been worked out. They are too numerous for inclusion in this paper and reference must be made to textbooks for the phase diagrams, for example, Lea and Desch (1956), Taylor (1964) and Bogue (1955). The help obtained from these books in writing this section is gratefully acknowledged. That portion of the quaternary system $CaO—Al_2O_3—Fe_2O_3—SiO_2$ that covers Portland cement has also been worked out. It is complicated and reference must be made to textbooks for the phase diagrams. No new compounds occur in the quaternary system which were not found in the binary and ternary systems. Part of the system $CaO—Al_2O_3—SiO_2$ is shown in figure 1. This diagram is shown in more detail in all modern textbooks on the chemistry of cement; the zone of Portland cement composition was also shown by Lea (1945). In calculating this area, the ferric oxide was added to the alumina and the sum of

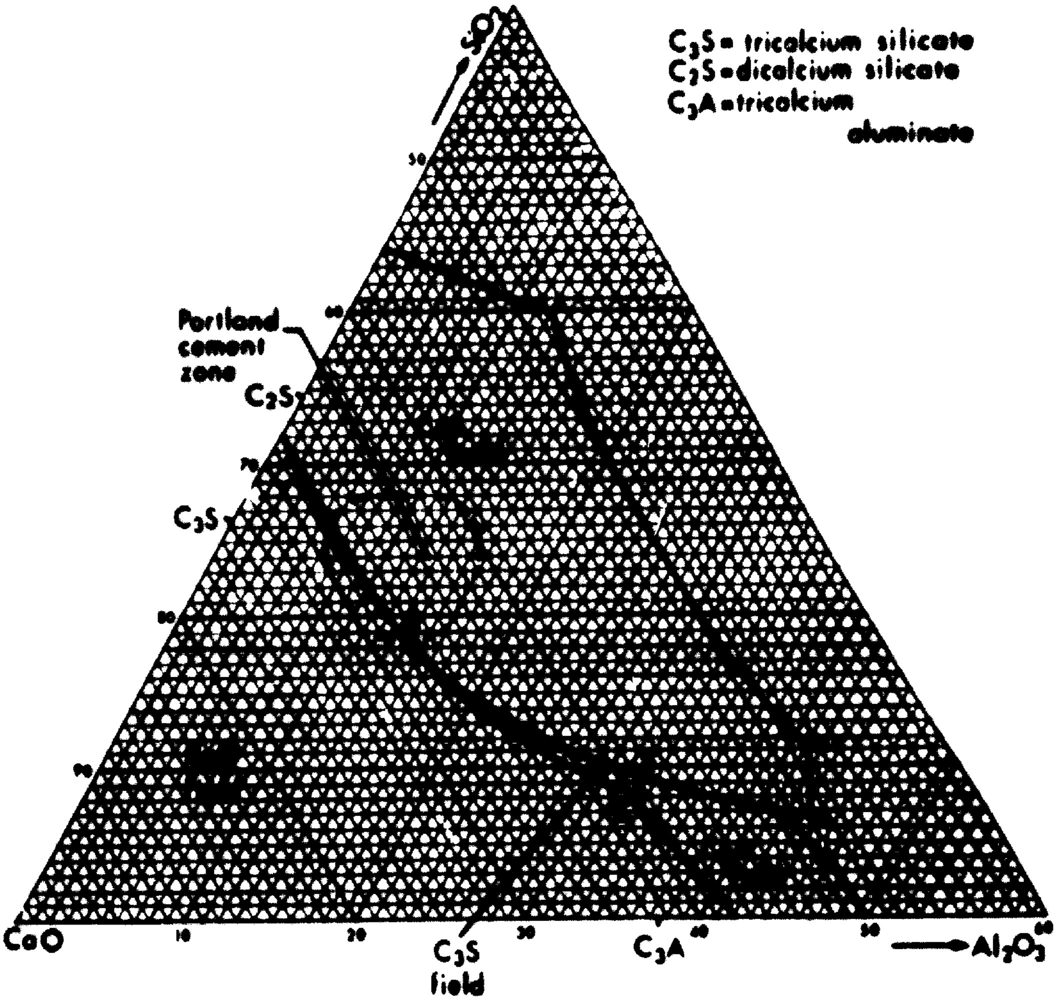


Figure 1. Phase diagram of system $CaO—Al_2O_3—SiO_2$
Source: Lea, 1945.

lime, silica, alumina and ferric oxide made up to 100 per cent. There may be objections to this procedure but it does give a relatively simple and reasonably accurate picture.

At point B (1,445° C) tricalcium silicate, dicalcium silicate and tricalcium aluminate exist in equilibrium with liquid and vapour. The liquid is saturated with all three solid phases. A change in concentration or temperature will upset the equilibrium, causing one of the solid phases to dissolve or the liquid to solidify. Hence B is a quintuple invariant point. Similarly C is a quintuple invariant point (1,470° C) at which CaO, tricalcium silicate and tricalcium aluminate are in equilibrium with liquid and vapour. A is also an invariant point where at 1,900° C tricalcium silicate decomposes into CaO and dicalcium silicate. The percentage compositions of these three invariant points are:

A		B		C	
CaO	68.4	CaO	58.3	CaO	59.7
Al_2O_3	9.2	Al_2O_3	33.0	Al_2O_3	32.8
SiO_2	22.4	SiO_2	8.7	SiO_2	7.5

It will be noted that the Portland cement area is relatively small. Actually, most modern cements contain more than 65 per cent CaO and therefore fall in that part of the cement area above the 65 per cent CaO line.

Microscopic, X-ray diffraction and other physico-chemical methods have established the presence of four major constituents in Portland cement clinker (table 1). They are constituents to be expected from the phase equilibria studies of the four major components to which reference has been made, but their relative proportions differ slightly from those expected in cooled clinker at equilibrium. This difference is due to one or more of these causes:

(a) Equilibrium is not quite attained during clinkering due to the slowness of the initial reactions between the solids and to the relatively small amount of liquid phase present in the clinker to provide a medium for the later reactions;

(b) Equilibrium is not maintained during clinker-cooling;

(c) Some of the liquid in the hot clinker is present in the cooled clinker as a glass, having failed to crystallize during cooling.

Lea and Desch (1956, p. 103) summarize the position: "Essentially we can regard Portland cement as a material which has closely approached equilibrium at the clinkering temperature, but which has cooled too rapidly to allow complete equilibrium to be established at the temperature of final solidification."

TABLE 1: MAJOR CONSTITUENTS IN PORTLAND CEMENT CLINKER

Compound	*Formula*	*Abbreviation*	*Composition (%)*
Tricalcium silicate	$3CaO\ SiO_2$	C_3S	$CaO = 73.69$ $SiO_2 = 26.31$
Dicalcium silicate	$2CaO\ SiO_2$	C_2S	$CaO = 65.12$ $SiO_2 = 34.88$
Tricalcium aluminate	$3CaO\ Al_2O_3$	C_3A	$CaO = 62.27$ $Al_2O_3 = 37.73$
Tetracalcium aluminoferrite	$4CaO\ Al_2O_3\ Fe_2O_3$	C_4AF	$CaO = 46.16$ $Al_2O_3 = 20.98$ $Fe_2O_3 = 32.86$

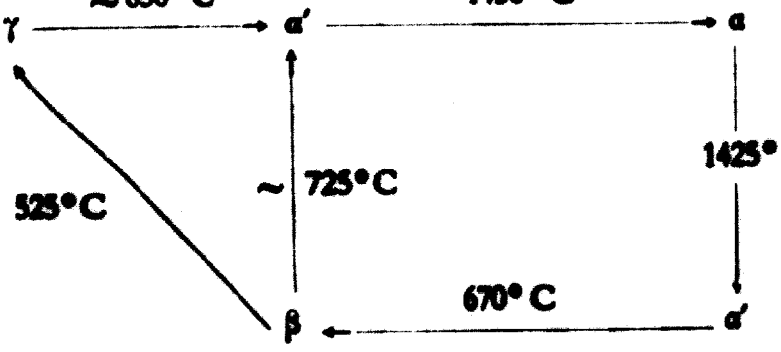
Brief notes on these compounds are given below.

Tricalcium silicate

Pure C_3S was for long thought to be stable only between 1,250° C and 1,950° C but it is now known to be stable up to 2,070° C, at which temperature it melts incongruently, giving CaO and a liquid. The range of stability includes the temperatures at which cement clinkering occurs during burning. Below 1,250° C, C_3S decomposes to give C_2S and free CaO but the rate of decomposition is very slow (Welch and Gutt, 1962, pp. 59—68). It is the most important constituent of Portland cement.

Dicalcium silicate

Pure C_2S occurs in four forms. The γ-form is stable at ordinary temperatures but changes on heating to the α'-form at about 830° C and the α'-form changes to the α-form at 1,450° C. On cooling, the α-form changes to the α'-form at 1,425° C and this changes to the β-form at 670° C which in turn changes into the γ-form at 525° C. The relationship between these forms has been summarized by Welch in this diagram:



The change from the β-form to the γ-form can be inhibited by small amounts of oxides such as B_2O_3 or Cr_2O_3. Oxides such as CaO, P_2O_5 and SO_3 can alter the inversion temperatures and might "stabilize" small quantities of the α'- or α-forms in cooled material, or delay or defer indefinitely the transformation of β-form to γ-form. The β-form of C_2S is the second most important constituent of Portland cement and is the form in which C_2S usually occurs in cement clinker, although the γ- and α'-forms are said to have been detected in cements.

Tricalcium aluminate

C_3A melts with decomposition at 1,535° C but is stable under clinkering conditions. Other calcium aluminates such as CA and C_5A_3 (now regarded as $C_{12}A_7$) are probably formed in early reactions in the kiln but disappear during later reactions and are not normally found in Portland cement.

Tetracalcium aluminoferrite

A ternary compound of CaO, Al_2O_3 and Fe_2O_3, known as Brownmillerite, was for many years thought to be a compound with the composition $4\,CaO \cdot Al_2O_3 \cdot Fe_2O_3$. However, it is now known that a series of solid solutions exits between $2\,CaO \cdot Fe_2O_3$ and $2\,CaO \cdot Al_2O_3$ (which is otherwise not known), of which the limiting composition is $6\,CaO \cdot 2\,Al_2O_3 \cdot Fe_2O_3$. The solid solution C_4AF may be a special point in this series; clinker composition is still expressed in terms of C_4AF.

The proportions in which the four major components occur in cement vary appreciably with relatively small changes in cement analysis but can be of this order:

	Per cent
C_3S	45—55
C_2S	15—25
C_3A	12—15
C_4AF	7—12

A method for calculating the amounts of these constituents in cement is given in the appendix to this chapter.

C. HYDRAULIC PROPERTIES OF COMPOUNDS IN CEMENT

The four major components of cement have the following properties as cementing agents when tested in 1 : 3 sand mortars:

Compound	*Cementing quality of pure compound*
C_3S	Good. It has all the essential properties of Portland cement, the strength of which at ages up to 28 days is a function of C_3S content.

Compound	*Cementing quality of pure compound (cont'd)*
C_2S	*α- and α'-forms* appear to have only slight hydraulic properties. *β-form* sets slowly over several days, produces little strength for about 28 days but thereafter strength increases up to six months to approach equality with C_3S. This form is largely responsible for increase in strength of Portland cement after 28 days. As already stated it is the usual form present in cement. The others are of minor interest in normal Portland cement. *γ-form* has no hydraulic properties.
C_3A	Has slight hydraulic properties. Sets almost instantaneously with much heat evolution. Develops some strength at one day but shows no increase thereafter.
C_4AF	Has slight hydraulic properties. Sets rapidly (but slower than C_3A) with considerable heat evolution (less than with C_3A). Develops some strength.

It must be appreciated that the properties of these compounds when present in cement will not be identical with those of the pure compounds due to the presence of small amounts of other substances in solid solution in them, but the behaviour of the pure compounds is the best available guide to their behaviour in cement.

D. SPECIFICATION

Although cement specifications vary with the country of origin, British Standard specification BS 12 : 1958 is used here as a typical example of a specification to which a producer would be expected to conform. It should be pointed out, however, that a cement in the United Kingdom that just satisfies the specified compressive strength would be at a disadvantage because of customer insistence on the rapid development of early-strength in the concrete.

Fineness

The cement, when tested by the prescribed method, shall have a specific surface of not less than:

Ordinary Portland cement	2,250 cm^2/g
Rapid-hardening Portland cement	3,250 cm^2/g.

Chemical composition

Lime saturation factor

The lime saturation factor (L. S. F.) shall not be greater than 1.02 and not less than 0.66 when calculated by the formula:

$$\text{L. S. F.} = \frac{(CaO) - 0.7\,(SO_3)}{2.8\,(SiO_2) + 1.2\,(Al_2O_3) + 0.65\,(Fe_2O_3)} \qquad (1)$$

where each symbol in parentheses refers to the percentage (by weight of total cement) of the oxide, excluding any contained in the insoluble residue referred to below.

Insoluble residue

The weight of insoluble residue determined by the prescribed method shall not exceed 1.5 per cent.

Magnesia

The weight of magnesia contained in the cement shall not exceed 4.0 per cent.

Alumina—iron ratio

The ratio of the percentage of alumina to the percentage of iron oxide shall not be less than 0.66.

Sulphuric anhydride

The permitted content of total sulphur in the cement, expressed as SO_3, shall not exceed the appropriate figure in the following table:

Tri-calcium aluminate % by weight	Maximum total sulphur expressed as SO_3 % by weight
7 or less	2.5
greater than 7	3.0

The tri-calcium aluminate content is calculated by the formula:

$$C_3A = 2.65\ (Al_2O_3) - 1.69\ (Fe_2O_3) \qquad (2)^1$$

where the symbols have the same meaning as in (1) above.

Loss on ignition

The total loss on ignition shall not exceed 3 per cent for cement in temperate climates or 4 per cent for cement in tropical climates.

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[1] This formula is derived thus:
Fe_2O_3 is assumed to be present as C_4AF
Al_2O_3 present as C_3A
$= \text{total } Al_2O_3 - Al_2O_3 \text{ combined with } Fe_2O_3 \text{ in } C_4AF$
$= \text{total } Al_2O_3 - Fe_2O_3 \times \frac{102}{160}$
$= \text{total } Al_2O_3 - 0.64\ Fe_2O_3$
Ratio $C_3A/Al_2O_3 = \frac{270}{102} = 2.65$
Therefore C_3A present $= Al_2O_3 \text{ present as } C_3A \times 2.65$
$= (\text{total } Al_2O_3 - 0.64\ Fe_2O_3) \times 2.65$
$= 2.65\ .\ Al_2O_3 - 1.69\ Fe_2O_3.$

Strength

Compressive strength

Method (1). The average compressive strength of three mortar cubes, prepared, stored and tested in the prescribed manner shall be:

(*a*) Ordinary Portland cement
3 days (72 ± 1 hr) not less than 2,200 lb/in^2 (154 kg/cm^2);
7 days (168 ± 2 hrs) shall show an increase on the compressive strength at 3 days and be not less than 3,400 lb/in^2 (239 kg/cm^2);

(*b*) Rapid-hardening Portland cement
3 days (72 ± 1 hr) not less than 3,000 lb/in^2 (210 kg/cm^2);
7 days (168 ± 2 hrs) shall show an increase on the compressive strength at 3 days and be not less than 4,000 lb/in^2 (281 kg/cm^2).

Method (2). The average compressive strength of three concrete cubes, prepared, stored and tested in the prescribed manner, shall be:

(*a*) Ordinary Portland cement
3 days (72 ± 1 hr) not less than 1,200 lb/in^2 (84 kg/cm^2);
7 days (168 ± 2 hrs) shall show an increase on the compressive strength at 3 days and be not less than 2,000 lb/in^2 (140 kg/cm^2);

(*b*) Rapid-hardening Portland cement
3 days (72 ± 1 hr) not less than 1,700 lb/in^2 (119 kg/cm^2);
7 days (168 ± 2 hrs) shall show an increase on the compressive strength at 3 days and be not less than 2,500 lb/in^2 (175 kg/cm^2).

Tensile strength

When specially desired, the one-day strength test of rapid-hardening Portland cement shall be asked for at the time of placing the order. When done as prescribed, the average tensile strength of six mortar briquettes shall not be less than 300 lb/in^2 (21 kg/cm^2).

Consistence of standard cement paste

The quantity of water needed to produce a paste of standard consistency shall be ascertained by the prescribed method. This quantity of water is used to determine the water content of the pastes used for setting time and soundness tests.

Setting time

The setting time of the cement, when determined by the prescribed method, shall be as follows:

Initial setting time: not less than 45 minutes;

Final setting time: not more than 10 hours.

Soundness

The cement, when tested for soundness by the prescribed method, shall not have an expansion of more than 10 mm (0.4 in).

E. COMMENTS ON SPECIFICATION FOR CHEMICAL COMPOSITION

Lime saturation factor

The L. S. F. is a measure of the "free" CaO content of cement (i. e., CaO not combined with SiO_2, Al_2O_3, Fe_2O_3 or SO_3). A considerable amount of free CaO in clinker may cause unsoundness in the cement resulting from expansion after setting due to its hydration to calcium hydroxide. It is, of course, common practice for builders to add hydrated lime ($Ca(OH)_2$) to cement, but this does not produce unsoundness because it is hydrated when used. Free CaO in cement clinker is present in crystal lattices and therefore hydrates slowly so that hydration is unfinished when the cement sets.

The maximum lime content which can be present without free lime appearing at the clinkering temperature in equilibrium with the liquid phase is expressed by the formula:

$$CaO = 2.8 \times \%\ SiO_2 + 1.2 \times \%\ Al_2O_3 + 0.65\%\ Fe_2O_3 \qquad (3)$$

To this must be added the lime equivalent to the SO_3 present, normally largely supplied by the gypsum added as a retarder $= 0.7\% \times \%\ SO_3$.

A high L. S. F. ensures a high C_3S content with quick development of early-strength. The specified limits for L. S. F. enable a high C_3S content to be achieved in the cement while ensuring that unsoundness will not develop due to free lime.

Magnesia

Unsoundness in cements due to expansion as a result of a high magnesia content has occurred and often becomes apparent only after long periods. The evidence is not unambiguous but there seems no doubt that the expansion due to free lime is increased at all ages of the cement by the presence of magnesia (Bogue and Lerch, 1945). A maximum limit for magnesia is therefore fixed to obviate any risk of failure.

Alumina/iron ratio

Alumina and ferric oxide act as fluxes in the kiln, increasing the liquid phase and reducing the clinkering temperature, but too high a proportion of these oxides can produce too much liquid in the kiln, with consequent ring or ball formation. The relative proportions of Al_2O_3 and Fe_2O_3 determine the amounts of C_3A and C_4AF in the clinker. C_3A, as stated in section C of this chapter, has an almost instantaneous set and the amount present in clinker must be restricted (normally below 18 per cent) or the cement will set too quickly. The lower the Al_2O_3/Fe_2O_3 ratio, the higher the proportion of C_4AF to C_3A. On the other hand, a proportion of C_3A helps the initial set of the cement and perhaps adds a little to the initial strength, although C_3S is by far the major contributor to early strength. The weight ratio Al_2O_3/Fe_2O_3 would have to fall to 0.64 (or, put the other way round, the Fe_2O_3/Al_2O_3 ratio would have to be 1.56) for all the Al_2O_3 to be present as C_4AF. A weight ratio Al_2O_3/Fe_2O_3 of 0.66 ensures that there is sufficient Al_2O_3 present to combine with all the Fe_2O_3 to give C_4AF and that some C_3A is also present in the cement. In practice, this ratio lies between 1.5 and 3.5 but combination in the kiln becomes more difficult as this ratio increases. A low Al_2O_3/Fe_2O_3 ratio gives too much liquid in the kiln, with consequent operational difficulties.

The ratio $SiO_2/(Al_2O_3 + Fe_2O_3)$, although not covered by specification, is important for kiln burning. It usually lies between 1.5 and 3.0 and combination becomes more difficult as the ratio increases, especially above 3.0.

Sulphuric anhydride

The amount of gypsum incorporated in cement as a retarder to control the setting time varies with the C_3A content. The presence of large quantities of gypsum leads to slow expansion in the set cement and the quantity in cement is therefore strictly limited.

F. PRODUCTION

Cement is manufactured by blending the raw materials to give a homogeneous mixture, burning the mixture in a rotary kiln to form a clinker which is ground with gypsum to produce cement. A line diagram is given in figure 2.

Raw materials

The main source of lime is calcium carbonate in the form of limestone or chalk. These materials often contain dolomite ($MgCO_3 \cdot CaCO_3$) but the amount present must be such that the MgO in the cement does not exceed 4 per cent. (See section D in this chapter.) Silica, alumina and ferric oxide are supplied as clay, marl or shale (the two latter may also contribute some calcium carbonate). Deficiencies of silica, alumina or ferric oxide in the raw materials

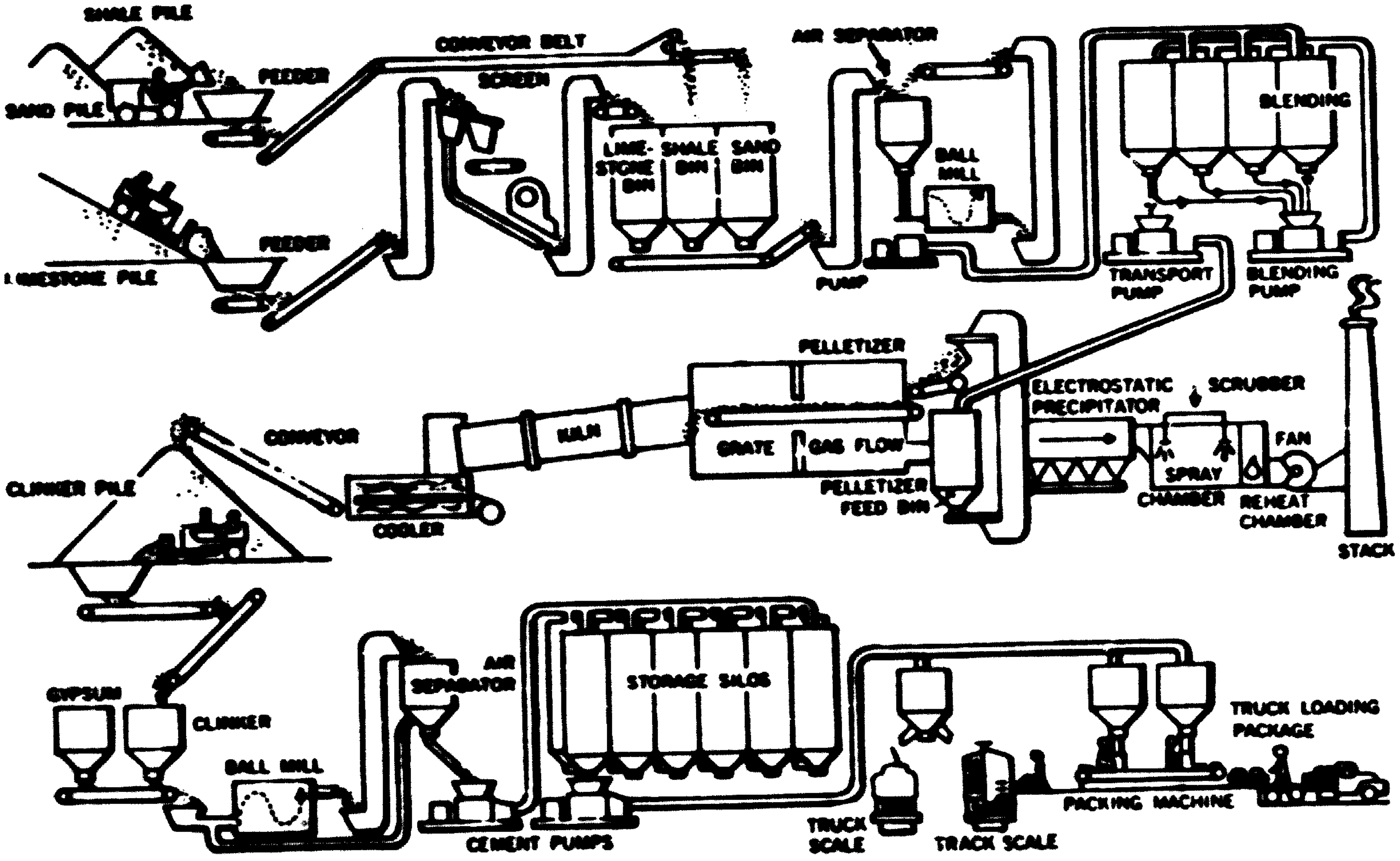

Figure 2. Line diagram of cement manufacturing process
Source: United Nations, 1963.

available can be rectified by the addition of sand, bauxite and a cheap form of ferric oxide such as pyrites cinders. If the kiln is fired by coal, allowance must be made for the silica, alumina and iron oxide introduced by the coal ash into the burden. Some of the sulphur present in the fuel will appear in the clinker as alkali metal sulphates and thus reduce the amount of gypsum that can be added as a retarder.

Preparation of raw materials

The preparation of the raw materials depends on whether they are fed to the kiln as a mixture of dry powders (dry process) or as a slurry (wet process). Modern plants using hard limestone normally employ the dry process and the dry process is used in anhydrite kilns. The wet process will therefore not be further considered.

The raw materials must be accurately proportioned to give the required composition and finely ground to produce reasonably rapid rates of reaction between the solids in the kiln before the liquid phase appears. The raw materials are therefore crushed and dried, when necessary, and weighed into mills where they are ground and mixed. The dry, finely divided mixture, "raw meal", which leaves the mills is conveyed, usually by pneumatic conveyors, to storage silos which are also used as blenders to even out short-term fluctuations in the raw meal composition.

Calcination

Raw meal is taken from the storage silos to a rotary kiln, fired by pulverized coal, oil or gas, and travels through the kiln counter-current to the hot air flow. A kiln about 200 ft long by 14 ft in diameter would be required for an output of 350,000 tons per year clinker if modern heat recovery equipment were installed. The kiln would be much longer without heat recovery equipment. The time of passage through such a kiln is about 2½ hours, but the time in the clinkering zone probably does not exceed 20 minutes. The clinkering temperature is about 1,450° C and clinker leaves the kiln at 1,000° C +. It passes to coolers in which the air required for fuel combustion is preheated by heat from the clinker. The cooled clinker (about 100° C) is taken to clinker stores. Fairly rapid cooling of the clinker is desirable.

The kiln atmosphere normally contains an excess of oxygen so that the iron in the clinker is largely present as ferric iron. Reducing conditions in the kiln have undesirable effects on the clinker. Thus, the decomposition of C_3S to C_2S and CaO below 1,250° C is markedly accelerated, probably due to replacement of calcium in C_3S by ferrous iron. In addition, the tendency of C_2S to revert from β- to γ-form on cooling is increased.

One form of heat recovery is based on the use of raw meal which has been granulated with a small amount of water in a dish granulator. The granules are conveyed to the kiln, called a Lepol kiln, on a travelling grate and heat is recovered from the kiln exit gas by passing it through the granules on the travelling grate. This improves heat efficiency and is one acceptable method of reducing the fuel requirement. Some raw meals produce granules which are not sufficiently strong to survive the handling and heating on a Lepol grate.

The kiln is lined with ordinary firebricks in the relatively cool back end but these are attacked by the kiln burden in the hotter zones where more resistant bricks such as high alumina, magnesite or chrome-magnesite are required.

The heat balance in cement kilns has been studied by Gygi (1954, p. 750). He calculated that the heat theoretically required to form 1 kg of clinker was 429 kcal. The actual heat requirement will vary slightly with the composition of the raw meal. Because much heat is lost, chiefly by radiation from the kiln and in the kiln exit gases, the over-all heat efficiency of a modern dry cement kiln is at best 50 per cent, so that the actual heat requirement in the kiln is of the order of 860 kcal/kg clinker. Later workers give slightly different figures, but the theoretical heat requirement seems to be about 400 kcal/kg clinker. The actual heat requirement differs little from the figure of 860 kcal/kg clinker given above, but large kilns producing 1,000 tons clinker per day, or more, can achieve figures below 800 kcal/kg clinker (Münk, 1963). The heat required to dry the raw materials before preparing the raw meal must be added to this heat requirement.

A broad picture of the reactions occurring in a cement kiln is as follows:

500° C +	Release of combined water from clay
800°—900° C	Formation of C_2S begins
900° C	Decomposition pressure of $CaCO_3$ reaches 1 atmosphere
1,100°—1,200° C	C_3A and C_4AF formed
1,260° C	Liquid formation begins
1,260°—1,450° C	C_3S formed, with progressive reduction in free lime content.

The main function of Al_2O_3 and Fe_2O_3 is to act as fluxes, which reduce the clinkering temperature and make it easier to produce clinker with a high C_3S content without too much free CaO.

Clinker can be "overburned", that is, subjected to too high a temperature during clinkering with resultant increase in the amount of liquid. This impairs the properties of the cement, due probably to the higher "glass" content in the clinker, formed from cooling in the presence of increased liquid.

Heat recovery and effluent treatment

The temperature of the gas at the exit of a kiln designed for use without heat recovery equipment can be several hundred degrees centigrade and represents a considerable heat loss. Modern cement kilns are therefore usually equipped with heat recovery systems. These are so efficient that the temperature of the kiln exit gases is allowed to rise to 900°—1,000° C.

One heat recovery system, the Lepol kiln, has been mentioned in section F of this chapter, another system recovers heat from the kiln exit gases by using them to preheat the incoming raw meal in equipment such as the Humboldt suspension preheater and the Polysius Dopol preheater. In the Humboldt preheater, the kiln gases pass through four cyclones mounted one above another. The kiln gas enters the bottom cyclone and passes successively through the other cyclones. Raw meal is fed to the preheater before the top cyclone where it is entrained and heated by the kiln gas, from which it is recovered by the normal cyclonic action and passes to the next cyclone. The raw meal is thus preheated to 750°—800° C and the kiln exit gas cooled to 300°—350° C. Some decarbonation occurs in the preheater. Sufficient heat remains in the kiln exit gas for this to be suitable for use in drying raw materials. A high alkali content in the raw meal may cause operational difficulties in suspension preheaters due to build-up in them. Other manufacturers make equipment based on a single gas stream but Polysius has developed a Dopol preheater, in which the gas stream is split. In all these preheaters, the dust burden of the kiln exit gas increases during passage through the preheaters. The gas leaving the preheaters is therefore dedusted with electrostatic precipitators and the recovered dust returned to the kilns.

Use of the heat in the kiln exit gas has not only improved the heat efficiency of dry rotary kilns but has also helped to reduce kiln length.

Conversion of clinker to cement

Clinker is taken from the clinker stores to tube mills, where it is mixed with a small amount of gypsum and ground to a fine powder. The cement is conveyed pneumatically to storage silos, packed pneumatically, and the bagged cement is taken to a product store for despatch. Much of the cement may be despatched in bulk.

G. RAPID-HARDENING PORTLAND CEMENT

Rapid-hardening Portland cement is cement that develops a high early-strength. It is a development of ordinary Portland cement and there is no sharp division between the two cements.

Rapid-hardening cement is usually made by finer grinding of the clinker, although other changes are sometimes required.

H. CAPITAL COSTS

Much information in the next two sections is taken from a report on cement/nitrogenous fertilizers production based on natural gas (United Nations, 1963). It is subsequently referred to as the "1963 report". It is assumed in the present report that a developing country would, as far as possible, follow the trend in developed countries and install a plant with a large output. Data are given in the 1963 report for a dry kiln installation in a developing country with a capacity of 400,000 tons of cement per year. Since this data is readily available, it has been used in the present report.

Fixed capital cost

	tons of cement/year
Plant capacity	400,000
Plant output (90 per cent)	360,000

The plant output is based on American achievements (1963 report, p. 22). This may be optimistic for a developing country, but the output achieved depends, among other factors, on the amount of "spare" capacity built into the plant when it is designed.

The total fixed capital cost in 1960 of a dry kiln plant in a developing country with the above capacity is given in the 1963 report (p. 4) as $35.10 per ton per year. This cost covers the plant for all stages from raw material quarrying to cement packing. At the 1960 exchange rate, this is equivalent to £12.5 per ton per year. On the assumption that the United Kingdom cost index has risen by about 35 per cent since 1960, the 1968 cost in a developing country would be about £17 per ton per year. The total fixed capital would then be £6.8 million.

Working capital

In American plants, working capital (6 days) is about 3 per cent of fixed capital (1963 report, p. 22). A developing country would need to carry much higher stocks of machinery spares, refractory bricks and so forth and it is suggested that working capital in such countries should be taken as 10 per cent of fixed capital.

I. RAW MATERIAL AND OTHER REQUIREMENTS

Raw materials

Raw material requirements will obviously depend on the composition of the raw material available. The assumption has been made that limestone and shale (or clay) only are used as components of raw meal fed to the kiln and that 3 per cent gypsum is incorporated in the cement as a retarder. The quantities of limestone and shale for American plants are given in the 1963 report (p. 22) as 1.6 and 0.3 tons per ton of cement respectively. The limestone consumption seems rather high and a more usual figure would be 1.4 tons limestone per ton of cement, although the raw material consumption will depend on the alkali content which may prevent recycle of part or all of the recovered dust.

	tons/ton of cement
Limestone	1.4
Shale	0.3
Gypsum	0.03

All of these figures are on a dry basis.

Fuel

The fuel requirement in new dry cement plants in developing countries is given as 1,200 t cal per ton of cement (1963 report, p. 10). This is high for modern dry kilns with efficient heat recovery and a figure of 900 t cal per ton of cement is used on the cost summary below:

	t cal/ton of cement
Fuel	900

Electricity

The over-all electricity requirement from quarrying to cement packing for a dry kiln in a developing country is given as 120 kWh per ton of cement (1963 report, p. 10).

	kWh/ton of cement
Electricity	120

Maintenance

The maintenance cost is taken as 4 per cent of the total fixed capital. This, with an output of 360,000 tons of cement per year, is £0.75 per ton of cement.

	£/ton of cement
Maintenance	0.75

Labour

In a developing country the total personnel for a dry kiln plant with a capacity of 400,000 tons of cement per year is given as 442, of whom 95 are maintenance workers (1963 report, p. 21). The labour requirement will obviously depend on the degree to which mechanization and automatic controls are installed and could be much higher than this figure (cf. Indian labour requirements, 1963 report, p. 6). Accepting the total labour requirement given in the 1963 report, the number of maintenance workers in it must be deducted since the maintenance cost has already been expressed as a percentage of fixed capital. The residual labour requirement is 347 and, assuming that each employee works 42 hours per week (2,184 hours per year), the man-hour requirement is 2.1 per ton of cement at 360,000 tons per year output.

	man-hours/ton of cement
Man-hour requirements (less maintenance)	2.1

Depreciation

Depreciation in American plants of comparable capacity is about 7.5 per cent of fixed capital (1963 report, p. 23). It is suggested that depreciation in a developing country should be at the rate of 10 per cent of fixed capital which, at an output of 360,000 tons of cement per year, is about £1.9 per ton of cement.

	£/ton of cement
Depreciation	1.9

Packaging and transport

The cost of packaging for that proportion of the output which will be dispatched in bags and the cost of transporting the cement from the factory to the consumer must be estimated. These costs may be considerable.

Overhead costs

Overhead charges will be incurred and should be included in the cost estimates. A very approximate figure that can be used for preliminary evaluation is that the overhead charges are 100 per cent of the total labour cost.

Interest payments

The portion of the capital borrowed at a fixed rate of interest will normally have to be repaid in a specified period within the life of the plant. In addition, interest will be payable on the outstanding loan capital. The cost of servicing and repaying the loan capital must be included in the evaluation.

Return on equity capital

The return required on equity capital will depend on the source of this capital. Private enterprise will normally invest capital only if the estimates show a return on this capital comparable with the return available on alternative investments elsewhere. A developing country may itself provide equity capital, in which case the return on this capital may not be the only, or even the chief criterion, by which it judges where to invest. Nevertheless, the return on capital may help in deciding how to apportion limited capital resources between competing capital-intensive projects. Discounted cash flow calculations are needed as soon as the necessary data are available.

Summary

Requirements for production of one ton of cement:

Limestone (tons)	1.4
Shale (tons)	0.3
Gypsum (tons)	0.03
Fuel (t cal)	900
Electricity (kWh)	120
Maintenance (£)	0.75
Labour, excluding maintenance (man-hours)	2.1
Depreciation (£)	1.9
Overhead charges, approximately 100 per cent of labour costs	
Packaging and transport	to be added
Interest payments	
Loan repayments	
Return on equity capital	

A preliminary estimate of the total cost can be made from the data given above when unit costs and other factors are known. It must be emphasized that an accurate estimate can be made only by a contractor for a particular site that he has investigated in detail and for a particular production and sales pattern. The contractor will be able to supply estimates for commissioning charges and labour training which have not been included above.

APPENDIX

CALCULATION OF C_3S, C_2S, C_3A AND C_4AF PRESENT IN CEMENT

The method is due to Bogue (1929, p. 192).

Basic assumptions

(1) All the Fe_2O_3 reacts with CaO and Al_2O_3 to form C_4AF.
(2) The MgO remains substantially uncombined.
(3) The Al_2O_3 remaining after formation of C_4AF reacts with CaO to form C_3A.
(4) The remaining CaO reacts with SiO_2, forming C_2S. Any CaO then uncombined reacts with C_2S to form C_3S. CaO remaining after all the C_2S has been converted to C_3S will be present as uncombined CaO.

The assumptions presuppose that equilibrium is reached in the kiln. In practice, a small amount of CaO remains uncombined. The amount of free CaO must be determined by analysis and taken into account in calculating the cement composition.

The insoluble residue consists of quartz, SiO_2 and so forth but is usually small and not worth correcting for. If it is high, the SiO_2 content must be determined and deducted from the total SiO_2. The loss on ignition consists essentially of moisture and carbon dioxide that have been taken up by the cement after the clinker leaves the kiln. In calculating the cement constitution, this value is set down without further change.

Calculations

Each per cent of SO_3 combines with 0.70% of CaO to give 1.70% of $CaSO_4$

C1 = CaO equivalent of SO_3
= % $SO_3 \times 0.7$

Each per cent of Fe_2O_3 combines with 0.64% of Al_2O_3 and 1.40% of CaO to give 3.04% of C_4AF

a1 = Al_2O_3 equivalent of Fe_2O_3
= % $Fe_2O_3 \times 0.64$
C2 = CaO equivalent of Fe_2O_3
= % $Fe_2O_3 \times 1.40$
a2 = Al_2O_3 present in cement less a1
= Al_2O_3 available for combination as C_3A.

Each per cent of a2 combines with 1.65% CaO to give 2.65% C_3A

C3 = CaO equivalent of Al_2O_3 in C_3A
= a2 × 1.65
C = CaO available for combination with SiO_2
= CaO in cement less (uncombined CaO + C1 + C2 + C3)
S = SiO_2 in cement (unless corrected for SiO_2 in the insoluble residue).
S is first calculated to combine with CaO to form C_2S.

Each per cent S will combine with 1.87% CaO to give 2.87% C_2S

C4 = S + C − C_2S content as calculated above
= CaO available to combine with C_2S to give C_3S
% C_3S = 4.07 × C4
% C_2S = S + C − % C_3S

The first C_2S calculation (S × 2.87) is approximate only and is superseded by % C_2S = S + C−% C_3S.

This method of computing the compounds present in cement is illustrated below:

TABLE 2. COMPUTATION OF COMPOUNDS PRESENT IN CEMENT

Component	*Analysis*	*Free CaO*	*SO_3 equivalent*	*Fe_2O_3 equivalent*	*Al_2O_3 equivalent*	*C and S*	*C_3S*
CaO	62.8	0.3	C1 = 1.4	C2 = 4.8	C3 = 3.8	C = 52.5	—
MgO	3.7	—	—	—	—	—	—
Al_2O_3	4.5	—	—	a1 = 2.2	a2 = 2.3	—	—
Fe_2O_3	3.4	—	—	3.4	—	—	—
SiO_2	22.3	—	—	—	—	S = 22.3	—
SO_3	2.0	—	2.0	—	—	—	—
Loss	1.1	—	—	—	—	—	—
Insolubles	0.1	—	—	—	—	—	—
Free CaO	0.3	—	—	—	—	—	—
Ignition loss	Free MgO	—	$CaSO_4$	C_4AF	C_3A	C_3S	C_2S
1.1	3.7	—	3.4	10.4 say 10	6.1 say 6	44	30.8 say 31

C1 = CaO equivalent of SO_3
= 2 × 0.7 = 1.4%
a1 = Al_2O_3 equivalent of Fe_2O_3
= 3.4 × 0.64 = 2.2%
C2 = CaO equivalent of Fe_2O_3
= 3.4 × 1.40 = 4.8%
a2 = Al_2O_3 available for combination as C_3A
= total Al_2O_3 − a1
= 4.5 − 2.2 = 2.3%
C3 = CaO equivalent of Al_2O_3
= 2.3 × 1.65 = 3.8%

C = CaO available for combination with SiO_2
= total CaO—(free CaO + C1 + C2 + C3)
$= 62.8 - (0.3 + 1.4 + 4.8 + 3.8)$
$= 62.8 - 10.3 = 52.5\%$
C_2S = equivalent to S (per cent of SiO_2)
$= 22.3 \times 2.87 = 64.0\%$
C4 = CaO available to combine with C_2S to form C_3S
$= S + C - 64.0$
$= 22.3 + 52.5 - 64.0 = 10.8\%$
$C_3S = C4 \times 4.07$
$= 10.8 \times 4.07 = 44\%$
$C_2S = S + C - 44$
$= 22.3 + 52.5 - 44 = 30.8\%$

Subsequent work by Lea and Parker (1935), cf. Lea and Desch (1956), provided data from which the compound content of clinkers in which the equilibrium is assumed to be frozen from the clinkering temperature can be calculated. These data enable corrections to be applied to the values obtained by the Bogue method. Lea and Desch state that the complete calculation is somewhat tedious, but if a clinkering temperature of 1,400° C is assumed, approximate corrections for the Bogue method values for clinkers of Al_2O_3/Fe_2O_3 weight ratio 0.9 to 6.1 can be obtained from the equations given below. These corrections give values of the compound content accurate to ±2 per cent for a clinkering temperature of 1,400° C. They are not appreciably affected by the use of higher clinkering temperatures but may lead to rather larger errors for mixes clinkered at much lower temperatures. The equations shown below give the amounts to be added to the Bogue values on the assumption that the liquid present at the clinkering temperature crystallizes independently of any pre-existing solid. The corrections depend only on the Al_2O_3 and Fe_2O_3 contents of the clinker.

(a) Clinkers of Al_2O_3/Fe_2O_3 weight ratio 0.9 to 1.7

The Bogue values do not need correction.

(b) Clinkers of Al_2O_3/Fe_2O_3 weight ratio 1.7 to 6.1

The corrections to be added to the Bogue values are as follows:

C_3S: $+ (1.8\,[Al_2O_3] - 2.8\,[Fe_2O_3])$
C_2S: $+ (2.1\,[Fe_2O_3] - 1.4\,[Al_2O_3])$
C_3A: $+ (2.5\,[Fe_2O_3] - 1.6\,[Al_2O_3])$
C_4AF: Nil

The formula in square brackets is the percentage (by weight) of that compound in clinker.

For most clinkers and cements, the corrections to be added to the Bogue values are positive for C_3S and negative for C_2S.

The Lea and Parker data lead to the following equations for the compound content of normal clinkers and cements:

$C_4AF = 3.04\,[Fe_2O_3]$
$C_3A = 2.65\,[Al_2O_3] - 1.69\,[Fe_2O_3]$
$C_3S = 4.07\,[CaO] - 7.60\,[SiO_2] - 6.72\,[Al_2O_3] - 1.43\,[Fe_2O_3]$
$C_2S = 8.60\,[SiO_2] - 3.07\,[CaO] + 5.10\,[Al_2O_3] + 1.08\,[Fe_2O_3]$

Steinour (1957) replaces 5.10 by 5.07 in the equation for C_2S.

2. SULPHURIC ACID

A. Nomenclature

Sulphuric acid is produced by the addition of water to sulphur trioxide, $SO_3 + H_2O \longrightarrow H_2SO_4$.

Plant outputs, consumptions and the like are usually expressed as 100 per cent H_2SO_4, sometimes called monohydrate (M. H.); this procedure is followed in this report. SO_3 dissolves readily in sulphuric acid to form oleum. The oleum strength is defined as the percentage of free SO_3 in the acid; for example, 10 per cent oleum contains 10 per cent of free SO_3.[2]

The nomenclature of sulphuric acid varies from country to country. In the United Kingdom the usual grades of sulphuric acid available contain 77 per cent and 95—96 per cent H_2SO_4 and are known as brown oil of vitriol (B.O.V.) and rectified oil of vitriol (R.O.V.) respectively. B.O.V. is the maximum concentration normally produced by the Chamber manufacturing process (see section C in this chapter) and is near the minimum concentration which can be handled in mild steel equipment. R.O.V. is approximately the maximum concentration which can be made by heating B.O.V. One advantage of these two concentrations is that their freezing points are well below 0° C and they can therefore be handled in cold weather without freezing. The two most important grades of oleum contain 20 per cent and 65 per cent of free SO_3 respectively and also have freezing points below 0° C.

B. Specification

The specification is usually agreed between producer and customer to suit the use to which the sulphuric acid will be put. There is no all-embracing specification as in the case of Portland cement. Customers using sulphuric acid for batteries or in textile or foodstuffs manufacture will specify limits for iron,

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[2] The composition of 10 per cent oleum at 15.5°C is as follows:

Total SO_3 = 83.47 per cent

Therefore H_2O = 16.53 per cent

H_2SO_4 equivalent to 16.53 water $= 16.53 \times \frac{80}{18}$ as SO_3.

$= 73.47$

Therefore % of free SO_3 $= 83.47 - 73.47$

$= 10.$

sulphur dioxide, nitrogen oxides, arsenic, lead, fluorine and so forth, but those using it for fertilizer manufacture are unlikely to impose stringent limits for such impurities. Production of some high grades of sulphuric acid may require minor plant alterations (such as the use of iron-free packing in the drying and absorption towers). The qualities of acid required should therefore be discussed with the plant contractor before the plant design is finalized but it must be emphasized that any modifications to the standard design will increase the capital cost of the plant.

C. MANUFACTURE

The basic raw material for sulphuric acid manufacture is sulphur dioxide (SO_2). This is oxidized to sulphur trioxide (SO_3) which is then combined with water to produce sulphuric acid. In the earlier sulphuric acid plants, SO_2 was oxidized to SO_3 in lead chambers in the presence of nitrous gases (chamber process) but, as stated earlier, the maximum concentration of sulphuric acid obtainable in the chamber process is about 77 per cent H_2SO_4. In recent years the lead chambers have been replaced by towers (as in the Petersen and Kachkaroff processes) which produce acid containing about 80 per cent H_2SO_4. This is adequate for some consumers but more concentrated sulphuric acid or oleum is required in many modern processes. The concentration of 77 per cent H_2SO_4 by heat is costly and unattractive and it is easier and cheaper to make 96 per cent H_2SO_4 and dilute this with water if lower strengths are required; 96 per cent H_2SO_4 and oleum are produced by the contact process in which gas containing SO_2 and an excess of oxygen (O_2) is brought into "contact" with a catalyst to form SO_3. Most sulphuric acid is now made in contact plants and the chamber and tower processes will not be considered further in this report.

Oxidation of sulphur dioxide

Thermodynamics of SO_2 oxidation

The reaction between SO_2 and O_2 to form SO_3 is exothermic, about 23,000 cal/g mole SO_3 being liberated at the temperature at which the reaction is carried out commercially. The conversion of SO_2 to SO_3 is a balanced reaction

$$SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons SO_3$$

The equilibrium constant of this reaction at constant pressure, K_p, is:

$$K_p = \frac{(p\,SO_3)}{(p\,SO_2)(p\,O_2)^{\frac{1}{2}}} \qquad (4)$$

Where p = the partial pressures in atmospheres of the three gases.

The equilibrium SO_3 partial pressure $(p\,SO_3) = K_p \times (p\,SO_2) \times (p\,O_2)^{\frac{1}{2}}$. In commercial operation the object is to convert as much SO_2 to SO_3 as is economically practicable. The SO_2 equilibrium partial pressure will therefore be low and high conversions of SO_2 to SO_3 are accordingly achieved by operating with an excess of O_2 and at a temperature which gives as high a value of the equilibrium constant as is practicable.

Values of this equilibrium constant at various temperatures were first determined by Bodenstein and Pohl (1905, p. 373), and the latest data derived from a paper by Evans and Wagman (1952) and given in Duecker and West (1959, p. 136) are reproduced in table 3 below. The help given by this textbook is gratefully acknowledged.

TABLE 3. VALUES OF EQUILIBRIUM CONSTANT AT VARIOUS TEMPERATURES

Temperature (°K)	ΔH_T kcal/mole	ΔF_T kcal/mole	$\log_{10} K_p$	K_p
600	−23.42	−9.94	3.621	4,180
700	−23.27	−7.72	2.410	237
800	−23.08	−5.51	1.505	32
900	−22.87	−3.34	0.811	6.47
1,000	−22.61	−1.18	0.258	1.81
1,100	−22.35	+0.96	−0.191	0.645
1,200	−22.06	+3.07	−0.559	0.276

ΔH_T = heat of reaction in kcal at the temperatures T in the table;

ΔF_T = Helmholtz free energy and represents the maximum work the system can perform at temperatures T.

ΔF_T is related to the equilibrium constant by the equation

$$\Delta F_T = -RT \log_e K_p. \tag{5}$$

where R = the gas constant = 1.98 g cal/g mole
ΔF_T = free energy in gram calories
T = temperature in ° K.
Columns 4 and 5 in table 3 can be derived by solving the equation

$$\Delta F_T = -2.3026 \quad RT \quad \log_{10} K_p.$$

A plot of K_p versus the reciprocal of the absolute temperature gives a straight line described by the equation:

$$\log K_p = \frac{4.955}{T} - 4.678 \tag{6}$$

Where T = temperature in ° K.

This equation has been used to calculate the variation of K_p with temperature. The results, to the nearest whole number, are given in table 4 following.

TABLE 4. VARIATION OF K_p WITH TEMPERATURE

Temperature (°C)	K_p	Temperature (°C)	K_p
300	9,363	450	150
325	4,072	475	89
350	1,894	500	54
370	934	525	35
400	485	550	22
425	264	600	13

For a given SO_2 concentration, the oxidation of SO_2 to SO_3 is obviously critically dependent on the temperature of the system. The temperature of the gases leaving the oxidation stage (conversion) must be as low as practicable to achieve maximum conversion of SO_2 to SO_3. The effect of temperature and O_2/SO_2 ratio on conversion of various gas mixtures is shown in figure 3. The approximate O_2 contents corresponding to the SO_2 figures given in figure 3 are obtained by subtracting the SO_2 content from 21. (This calculation applies only to gas from a sulphur burner.)

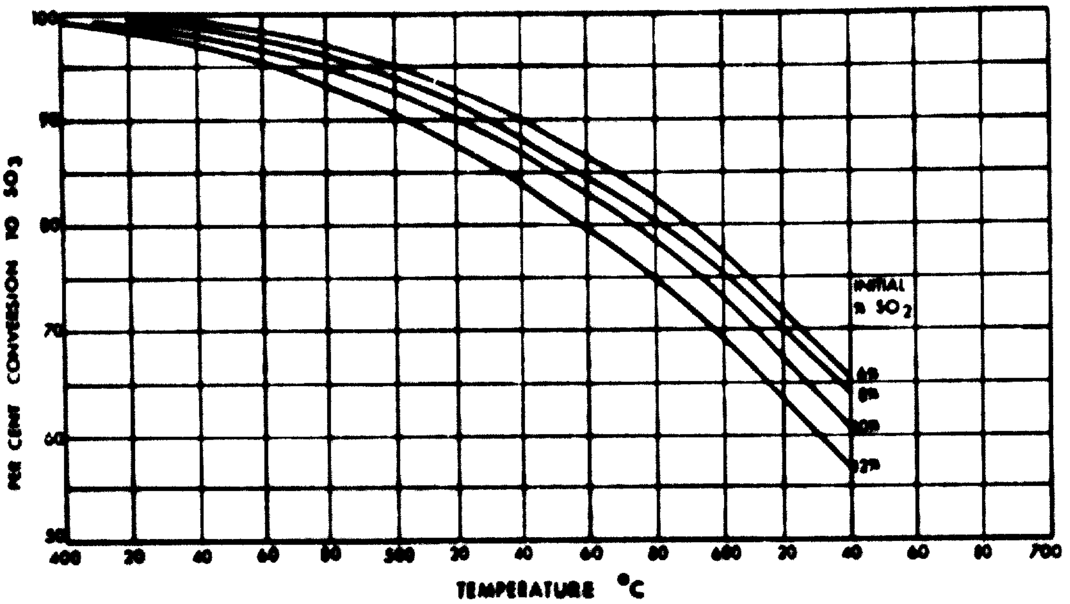

Figure 3. Equilibrium conversion of sulphur dioxide to sulphur trioxide for gas mixtures obtained by burning sulphur in air (concentration in volume per cent)
Source: Duecker and West, 1959, p. 161.

It will be seen from figure 3 that the high conversion required in commercial production can be obtained only at conversion exit temperatures below about 460° C.

Kinetics of SO_2 oxidation

It is necessary to consider the rate at which equilibrium is reached as well as the gas composition when the system is in equilibrium. The rate at which equilibrium is attained at acceptable values of K_p is too low for commercial use unless a catalyst is used to increase the reaction rate. The catalyst initially used was platinum, and this process is described by Bodenstein and Fink (1907) in their classical work. Commercial platinum catalysts were supported on asbestos, silica gel or calcined magnesium sulphate. The catalytic activity of platinum was adversely affected by a number of impurities liable to be present in small quantities in many sources of SO_2. This catalyst "poisoning", together with the high initial cost of the catalyst led to its replacement by vanadium catalysts, which are much less subject to poisoning and cost much less.

Vanadium catalysts contain vanadium pentoxide and potassium sulphate on a siliceous base. The alkali metal salt considerably increases the catalyst activity. Many kinetic studies of the oxidation of SO_2 in the presence of vanadium catalysts have been made and various rate equations have been proposed, but most of them are largely empirical and their theoretical basis is at best incomplete. Catalyst pellet size affects the reaction rate due to the limitation imposed by diffusion within the pores of the larger catalyst pellets. At higher temperatures, the chemical reaction rate is so fast that diffusion of gases to and from the catalyst surface becomes the rate-controlling factor. Because activation energy for gas diffusion is less than the activation energy for chemical reaction, the over-all activation energy for the process is lower at higher temperatures.

Textbooks and original papers must be consulted for further information on the reaction kinetics in the presence of vanadium catalysts. It is sufficient now to say that the velocity of the reaction increases rapidly with temperature. In commercial operation, it is necessary to balance the opposing effects of temperature on the equilibrium composition of the gas mixture and the rate at which equilibrium is attained.

Vanadium catalyst in SO_2 oxidation plants

The minimum temperature at which most vanadium catalysts are sufficiently active ("ignite") to give a reasonable reaction velocity is about 420°—430° C and they lose activity at a significant rate above about 600° C. Vanadium catalysts in production plants therefore operate between 420° and 600° C. The temperature of the gases leaving the conversion section must be kept as low as possible to achieve maximum conversion of SO_2 to SO_3. This is done by dividing the catalyst in the converter into three or four beds ("passes") with some form of heat removal between the passes. Most of the conversion is effected in the first two or three passes. The temperature rise in the last pass is therefore only a few degrees, thus giving the lowest practicable gas exit temperature. In practice, a catalyst manufacturer, knowing the characteristics of his catalyst, can calculate the optimum catalyst distribution between passes and the temperature ranges within which each pass should operate to achieve the required conversion efficiency. An equilibrium conversion diagram for a four-pass converter with vanadium catalyst working on 8 per cent SO_2 from a sulphur burner is given in figure 4. The cost of achieving equilibrium conditions in a production plant would be prohibitive because of the large amount of catalyst needed and the size of the

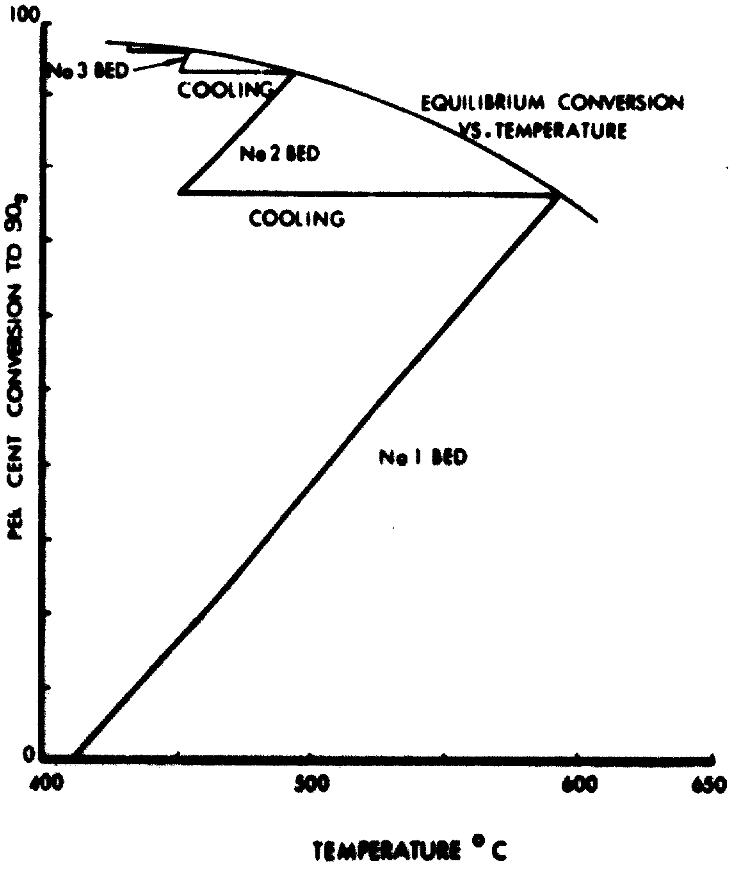

Figure 4. Equilibrium conversion diagram for four-pass vanadium catalyst system (using 8 per cent sulphur dioxide from a sulphur burner).
Source: Duecker and West, 1959, p. 163.

conversion equipment required. Conversion efficiencies 1—2 per cent below equilibrium are normally acceptable. The total volume of catalyst required in a converter depends on the composition of the gas entering it and may vary between 160 and 250 litres of catalysts per ton of H_2SO_4 per day.

Catalyst poisoning

Vanadium catalysts are much less susceptible to poisoning than platinum catalysts. For example, the amount of arsenic required to deactivate vanadium catalyst is 80,000 times the quantity which poisons platinum catalysts (Duecker and West, 1959, p. 183). However, vanadium catalysts are susceptible to fluorine poisoning. Fluorine and chlorine are said to cause volatilization of vanadium from the catalyst (Duecker and West, 1959, p. 184).

Another cause of difficulty with vanadium (and platinum) catalysts is dust deposited on the fast catalyst pass, which causes a high pressure drop across the bed and has to be removed by screening the catalyst. Some loss of catalyst occurs during this process and a small catalyst make-up is needed. The effect of dust deposition is largely physical and the catalyst is otherwise little affected.

Sources of SO_2 for sulphuric acid manufacture

SO_2 for sulphuric acid can be produced in the following ways:

(1) By the combustion of elemental sulphur;
(2) By roasting sulphur-bearing materials such as iron pyrites;
(3) As a by-product from metallurgical processes;
(4) From anhydrite;
(5) From other relatively minor sources.

The production of sulphuric acid from these various sources is briefly described below.

(1) *Sulphuric acid manufacture from SO_2 made by combustion of elemental sulphur*

Sulphur is melted, filtered if necessary, and pumped to a burner where it meets combustion air which has been dried with sulphuric acid to avoid mist formation in later stages of the process. The gas leaving the burner contains 10 — 11 per cent of SO_2 and 11 — 10 per cent of O_2 and is at a temperature of 900° — 950° C. Most of this hot gas passes through a waste heat boiler to recover as much as possible of the heat in a useful form and to reduce the gas temperature to that required in the conversion plant. The exit gas temperature is controlled by a bypass round the boiler. The gas passes through a filter packed with quartz or silica to remove dust before entering the converter. Much heat is evolved during the passage of the gas through the first catalyst bed and this is recovered by passing the gas through another waste heat boiler. The heat produced by passage through the second and third passes can be removed in steam superheaters or by injecting cold dried air into the gas stream. The cooling air added to the converter (or before it if air cooling is not used) is equivalent to producing a converter inlet gas containing about 8 per cent SO_2 and 13 per cent O_2 (O_2/SO_2 ratio = 1.6). Over 98 per cent of the SO_2 in this gas would be converted to SO_3 in a four-pass converter. The gas leaving the last pass is first cooled in an economizer which preheats the boiler feed water or in a heat exchanger in which the air for the sulphur burner is heated, and finally in an air cooler.

SO_3 in the cooled gas is dissolved in 98 — 99 per cent H_2SO_4 in an absorber to which dilute acid from the drying tower and water are added to maintain the concentration at 98 — 99 per cent H_2SO_4. The partial pressures of SO_3 and H_2O are at a minimum above acid of this concentration. The maximum amount of SO_3 can therefore be removed from the incoming gas and the minimum quantity of H_2O passed forward in the exit gas, thus minimizing the possibility of mist formation. If oleum is required, SO_3 is absorbed in 98 — 99 per cent of H_2SO_4 in a smaller tower before the main absorber, and absorber acid is fed to the oleum tower to maintain the required oleum strength. Production of oleum containing more than 35—40 per cent of free SO_3 is impossible at the SO_2 concentrations in the gas normally produced in the sulphur burner; 65 per cent oleum if required can be made by boiling 35 per cent oleum, condensing the SO_3 evolved and adding it to fresh 35 per cent oleum. The stack from a properly operated sulphur-burning plant is usually acceptable without further treatment, provided the bitumen in the sulphur does not exceed about 0.4 per cent. Bitumen, if present in sulphur, is oxidized to carbon dioxide and water when the sulphur is burned and the water combines with SO_3 to produce acid mist. The capital cost estimate given in section D of this chapter does not include any form of tail gas treatment. A simplified line diagram is shown in figure 5.

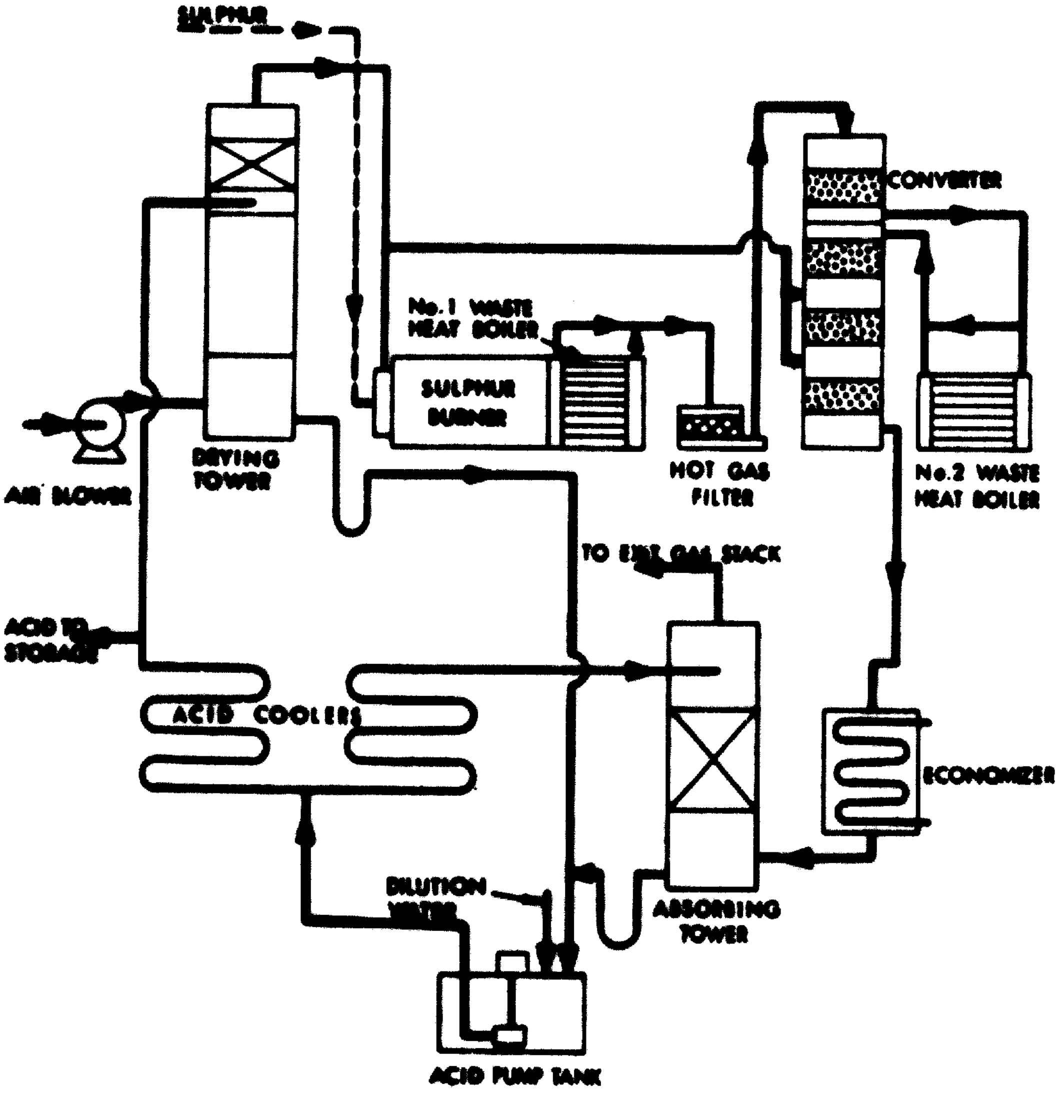

Figure 5. Sulphur-burning contact plant

(2) *Sulphuric acid manufacture from SO_2 made by roasting pyrites*

Iron pyrites consist of one or both of the iron sulphides FeS_2 (pyrite) and Fe_7S_8 (pyrrhotite). When heated in air, these sulphides are converted into ferrosoferric oxide and SO_2.

$$3\,FeS_2 + 8\,O_2 = Fe_3O_4 + 6\,SO_2$$

This reaction goes to completion at 900° C if the stoichiometric amount of O_2, or slightly more, is used. An oxygen deficiency causes some sulphur to remain in the calcine while an excess of oxygen (more than 10 per cent) converts the Fe_3O_4 to Fe_2O_3.

$$4\,Fe_3O_4 + O_2 = 6\,Fe_2O_3$$

At lower calcination temperatures, the oxygen needed to produce a substantially sulphur-free Fe_3O_4 calcine increases sharply; SO_3 can be formed during calcination from SO_2 and O_2 and any SO_3 so produced is lost during the subsequent gas cleaning operations. As previously explained in section C of this chapter, the SO_3 formed can be minimized by calcining at a sufficiently high temperature in the presence of a small amount of excess O_2. Very little SO_3 can be produced at 900° C and minimum SO_3 formation with good desulphurization is achieved by calcining at about 900° C in the presence of not more than 5 per cent of excess O_2.

The SO_2 concentration in the gas produced by roasting pyrites is lower than in the gas obtained by burning sulphur (for the same oxygen content). This is because oxygen is required to combine with the iron as well as the sulphur in pyrites, with a consequent increase in the nitrogen content of pyrites gas and corresponding decrease in its SO_2 content. Pyrites available in world markets usually contain 48 — 50 per cent of S and gas made from such material can contain 12 — 14 per cent of SO_2 with a small amount of oxygen, but the actual SO_2 concentration depends on the calcining equipment used (see below). The oxidation of pyrites is strongly exothermic and steam is usually raised by passing the hot gas from the roaster through a waste heat boiler.

A variety of equipment is available for roasting pyrites, such as the Badische Anilin Turbulent Layer Roaster, the Nichols Freeman Flash Roaster and the Nichols Herreschoff Hearth Roaster. The Turbulent Layer Roaster can receive pyrites up to 6 mm in size. Pyrites are roasted over a horizontal grate and the material is kept in motion by an air blast. The SO_2 content of the exit gas produced by burning pyrites containing 48 per cent S is 12 — 13 per cent. The Nichols Freeman Flash Roaster was developed to treat finely divided flotation pyrites, which are injected into the top of a large cylindrical combustion chamber and roasted while suspended in air. The exit gas contains about 10 per cent of SO_2. The Nichols Herreschoff Hearth Roaster has been used for many years. It consists of a number of circular firebrick hearths in a vertical casing. Pyrites are fed to the top hearth, propelled across it by arms with ploughs and dropped on to the hearth below. The exit gas contains 7 — 8 per cent of SO_2. The capital and maintenance costs are usually less than those of a Turbulent Layer or Flash Roaster, but the lower SO_2 concentration increases the cost of the subsequent gas purification plant and heat is not recovered from the hot gas. A recent development is the addition of equipment to recirculate part of the hot exit gas to the roaster. A hearth roaster with recirculation produces gas containing 10 — 11 per cent of SO_2 and heat is recovered from this gas in a waste heat boiler. The hot gas is recirculated from the outlet of the boiler. In all cases, the iron oxide residue ("cinders") is recovered and can be used in blast furnaces for pig iron production. The credit obtainable for pyrites cinders depends on local circumstances, but is usually about £2 to £3 per ton of cinders.

The SO_2 containing gas from all pyrites roasting equipment contains dust and other impurities (such as the volatile oxides of other metals present in the pyrites) which must be removed before the conversion section. Two methods can be employed to clean the gas after the coarser particles (the bulk of the dust content) have been removed in cyclones. In one, the gas passes through a Peabody Scrubber where it is cooled and almost all the remaining solid impurities are removed by water washing. The water leaving the Peabody Scrubber is blown with air to remove dissolved SO_2 and then put to drain. The SO_2 containing air joins the main gas stream which enters electrostatic mist precipitators for final cleaning, is dried by sulphuric acid and passes to the conversion plant. This is the cheapest method of gas cleaning where facilities exist for disposing of the effluent from the Peabody Scrubber. Where such facilities are lacking, the alternative cleaning method must be used. In this, the gas from the cyclones is taken to electrostatic dust precipitators and then to two towers, the first an unpacked spray tower and the second a packed cooling tower. Dilute sulphuric acid, usually containing about 20 per cent H_2SO_4, is circulated round each tower and becomes contaminated with the impurities removed. The disposal of this dirty acid may be difficult. The gas leaving the packed tower goes to an electrostatic mist precipitator and drying tower before entering the conversion plant.

It will be seen that the simple gas cleaning equipment of a sulphur-burning plant has been replaced by an elaborate gas cleaning system in which the gas is saturated with water vapour. Further, the gas in a sulphur-burning plant leaves the hot gas filter at the correct temperature for conversion, but the gas from a pyrites plant has been cooled virtually to atmospheric temperature and must be reheated to 420° C before entering the converter. This is done in a series of heat interchangers in which the hot gas leaving the converter passes is used to preheat the incoming gas. A preheater is installed to heat the converter when the plant starts up. In addition, air is added to the gas entering the drying tower to give an O_2/SO_2 ratio of about 1.5. The SO_2 concentration of gas entering the converter is therefore only about 7 per cent, irrespective of the type of pyrites roaster used: 98 per cent of the SO_2 in this gas would be converted to SO_3 in a four-pass converter. The SO_3 produced is absorbed in sulphuric acid as in a sulphur-burning plant and oleum may similarly be made but the proportion of total make which can be produced as oleum is less than in a sulphur-burning plant because of the higher moisture content of the purified SO_2 gas from a pyrites plant.

The gas leaving the absorber contains small amounts of unconverted SO_2 and unabsorbed SO_3, together with acid mist. It can usually be discharged to the atmosphere without further treatment, apart from the installation of an inexpensive mist eliminator. If desired, the SO_2 content of the stack gas can be reduced by scrubbing with water, or ammonia as a solution of ammonium sulphite and bisulphite, or with caustic soda as a solution of sodium sulphite and bisulphite. The latter two are economic only if there is a demand for the resulting ammonium or sodium salts. Any of these forms of scrubbing can reduce the total acidity in the stack gas to less than 2.3 g/m^3 but none can guarantee a stack of good appearance. Washing with an aqueous solution may cause the appearance of the stack to deteriorate because the combination of water vapour with SO_3 gives rise to a persistent mist which can be removed adequately only by electrostatic mist precipitators. The capital cost estimate given in section D of this chapter does not cover the installation of mist precipitators but the layout

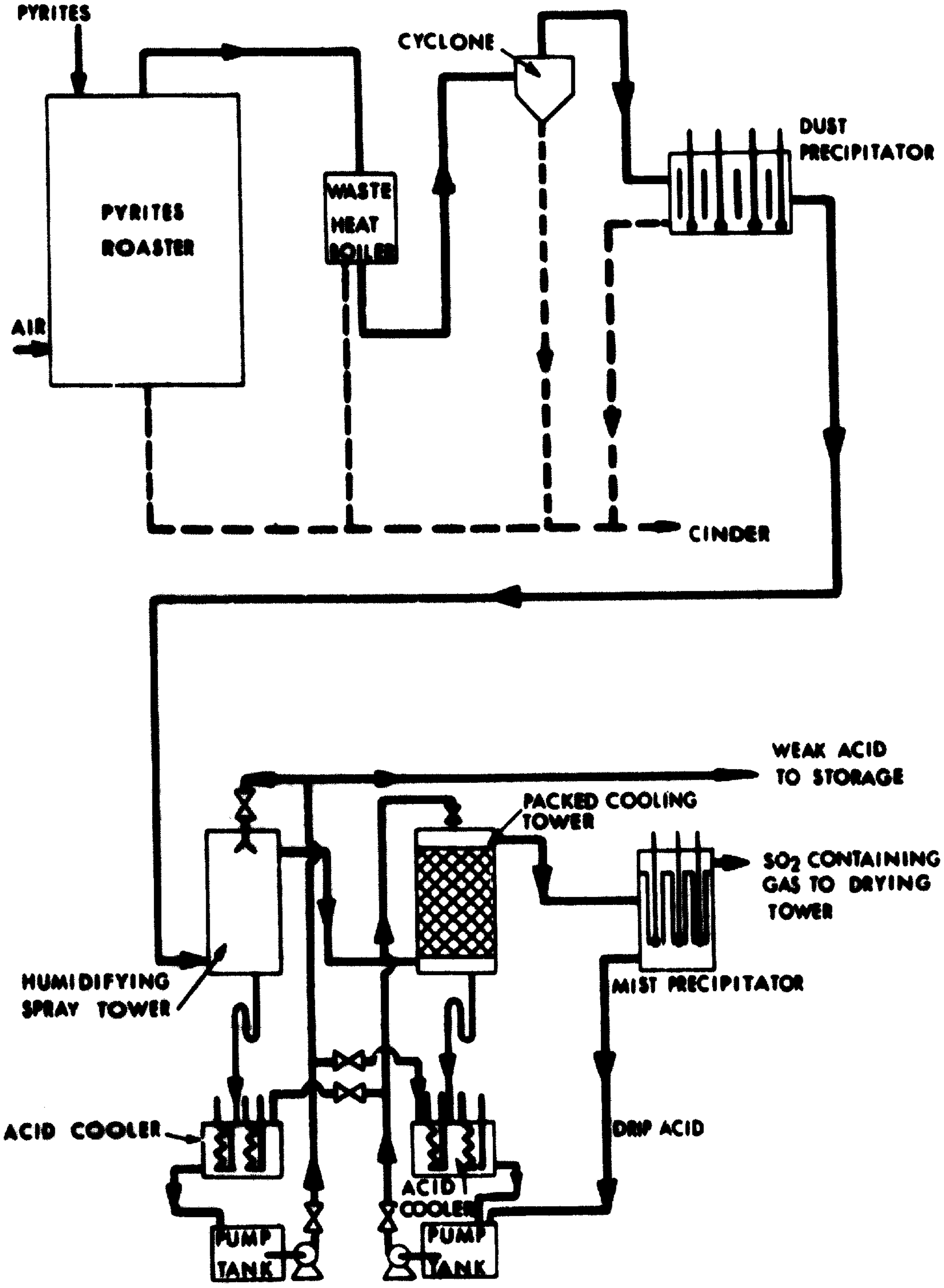

Figure 6. Pyrites plant: gas production and purification

should be planned to permit their subsequent installation if circumstances made this necessary.

Simplified flow sheets for the production of sulphuric acid from pyrites are given in figures 6 and 7.

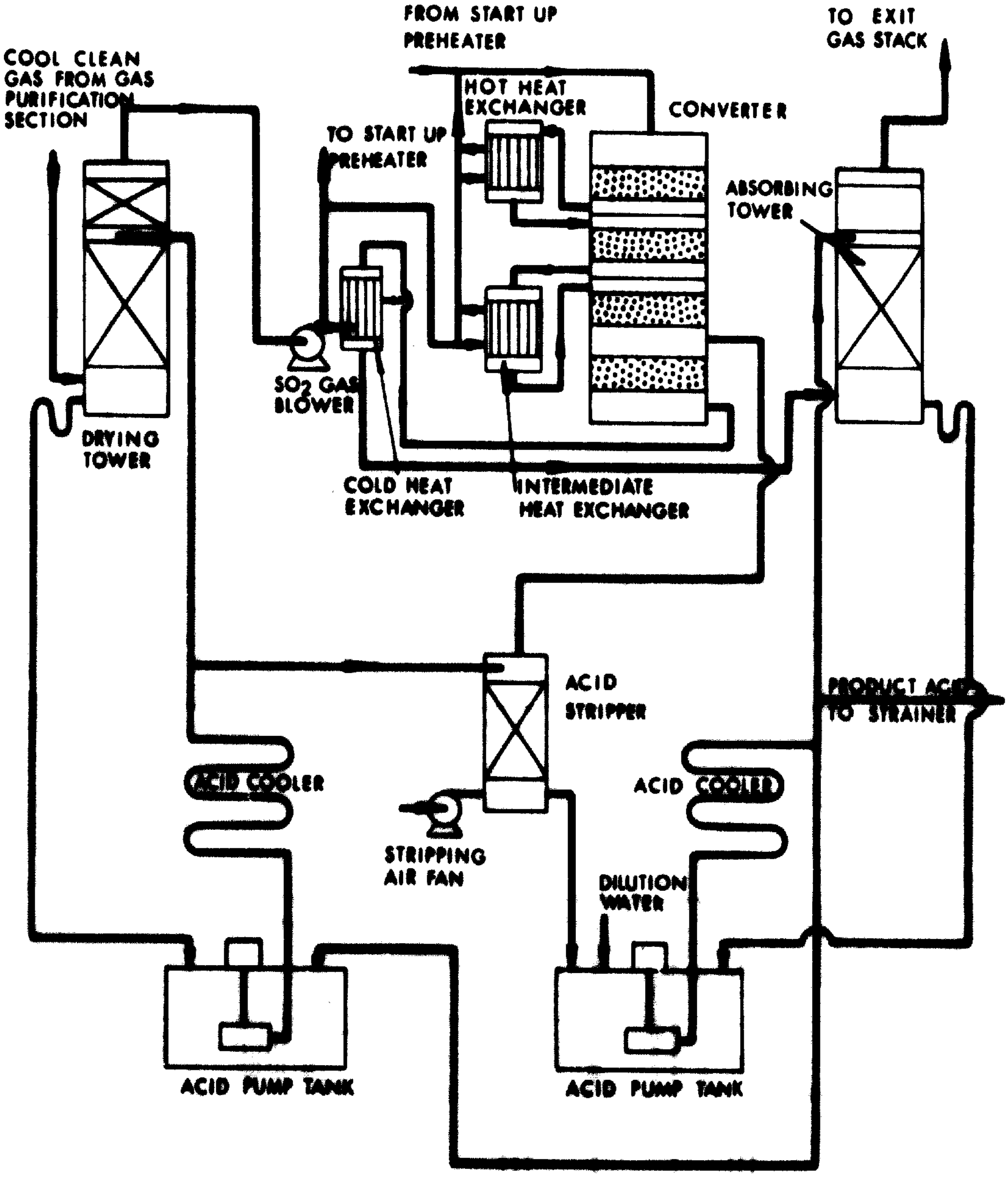

Figure 7. Pyrites plant: SO_2 oxidation and absorption

(3) *Production of sulphuric acid from SO_2 made as a by-product of metallurgical processes*

The production of copper and zinc from their sulphide ores involves roasting with simultaneous production of SO_2 as a by-product. This SO_2 can be converted to sulphuric acid by the same process as that used for SO_2 obtained from roasting pyrites, but whereas pyrites are roasted primarily to produce SO_2, the sulphides of copper and zinc are calcined primarily as a step in the recovery of the metals. Hence a producer of copper and zinc usually supplies SO_2 into his sulphuric acid plant at nil cost. He may even regard the SO_2 as having a negative value because it cannot be discharged direct to the atmosphere. Hence by-product SO_2, when available, enables sulphuric acid to be made at low cost.

(4) *Production of sulphuric acid from SO_2 made from calcium sulphate*

This is dealt with in chapter 3 of this report.

(5) *Production of sulphuric acid from other SO_2 sources*

SO_2 can be made by:

(a) Decomposition of petroleum refinery sludge;
(b) Burning hydrogen sulphide which is made as a by-product in various processes;
(c) Burning spent oxide made by removing hydrogen sulphide from town's gas or industrial gases.

These are relatively small and specialized sources of SO_2 and none is considered further in this paper.

D. CAPITAL COSTS

It is clearly impossible to give accurate cost estimates for plants erected on unknown sites. The cost of a plant in a developing country will depend on the engineering facilities and skills available and an accurate estimate can be produced only by an engineering contractor for a specific site that he has investigated. Order of cost estimates are given below solely for the preliminary evaluation of a project and for indicative comparisons of the cost of making sulphuric acid by various routes.

The costs are given as battery limit costs for the United Kingdom. A developing country would have to add to the battery limit price the cost of transport which might amount to 10 — 15 per cent of the battery limit cost. In addition, the price of civil and erection work may be higher in a developing country than in the United Kingdom. An increase of 30 per cent in the cost of this work would amount to about 10 per cent of the battery limit cost.

It must also be remembered that considerable capital costs must be incurred outside the battery limit to provide an operating factory. These costs which are known as offsites, vary greatly with the site, commercial and policy requirements. Items to be considered include: site purchase; site cleaning and levelling; piling or rock removal; roads and railways (both to the factory and within it); drainage and effluent treatment; power and water supplies and distribution network; power generation from surplus steam; packaged boilers; compressed air supply; raw material and product storage capacity: loading and unloading facilities and vehicles; offices and furniture; workshops and equipment; canteens, washrooms and changerooms and engineering stores.

Many of these depend on the geology and geography of the site chosen, but the size of raw material and product storage is determined by sales pattern, transport availability and reliability, while offices and other items depend on policy decisions, bearing in mind existing facilities and local building regulations.

No realistic estimates can be given in this paper, but it must be realized that these offsite costs are not insignificant and can range from 25 per cent of battery limit cost upwards and are sometimes two or three times higher.

All these additional costs must be included in the preliminary evaluation of a project. The battery limit costs given below include moderate storage for sulphuric acid and for pyrites. They do not include storage for sulphur or pyrites cinders nor do they contain any allowance for a difficult site. Costs less than those given are sometimes quoted in literature, but as Duecker and West (1959) point out, the cost of sulphuric acid made in a plant in which the prime objective has been a minimum capital cost will be greater than that made in a plant designed to achieve minimum operating costs.

Fixed capital cost estimates

These capital costs are order-of-cost estimates only.

Sulphur-burning plant

Running time: 350 days per year. Minimum economic size in developed country: 50,000 tons per year. Costs rounded off to nearest £50,000.

Output of 100% H_2SO_4		
tons/year	*tons/day*	*Battery limit cost (£)*
52,000	150	300,000
105,000	300	500,000
210,000	600	850,000

Pyrites plant

Running time: 340 days per year. Minimum economic size in developed country: 100,000 tons per year. Costs rounded off to nearest £50,000.

Output of 100% H_2SO_4		
tons/year	*tons/day*	*Battery limit cost (£)*
51,000	150	700,000
102,000	300	1,100,000
204,000	600	1,750,000

Working capital

The working capital should be taken as 10 per cent of the battery limit cost.

E. RAW MATERIAL AND OTHER REQUIREMENTS

Raw materials

	tons/ton of H_2SO_4
Sulphur (95 per cent efficiency)	0.345
Pyrites (48 per cent S at 91 per cent efficiency)	0.75

Steam and electricity

Steam is generated at all outputs quoted for both sulphur-burning and pyrites plants. This steam may be used to drive the main blower by steam turbine, to generate power or to be fed into the factory steam system. The choice between these depends on local factory circumstances.

Sulphur-burning plants

Steam: 1.0 — 1.2 tonnes/ton of H_2SO_4
Electricity: 35 — 50 kWh/ton of H_2SO_4
(assuming steam not utilized on plant).

Little electricity will be needed if steam is used to generate power or to drive the main blower.

Some steam will be required for sulphur melting, say 0.2 tonnes per hour.

Pyrites plant

Steam: 1.0 — 1.2 tonnes/ton of H_2SO_4
Electricity: 60 — 100 kWh/ton of H_2SO_4
(assuming steam not utilized on plant).

As with sulphur-burning plants, use of the steam generated within the plant can make these plants virtually self-sufficient in energy.

With both types of plants, the steam produced increases and the electricity used decreases with increased acid production. (Note: The capital costs do not include equipment for generating electricity from the steam produced.)

Water requirements

Cooling water is required to remove the heat generated by absorption of SO_3 in 98 — 99 per cent H_2SO_4. Cooling water requirements vary with differences in local temperatures and, to some extent, with plant design. It is therefore possible only to give a spread of cooling water requirements. These will be much reduced if a closed circulating water system is employed. Cooling water requirements will be appreciably higher in tropical or sub-tropical regions than in temperate climates.

The amount of boiler feedwater will depend on the amount of condensate returned to the boilers. "Dilution" water is needed if the product acid contains 94 — 98 per cent H_2SO_4.

	Requirement per ton of H_2SO_4	
	Sulphur burning	*Pyrites*
Cooling water (m^3)	9 — 18	27 — 72 (with weak acid circulation system)
Boiler feed water (m^3) (with nil condensate return and 10% blowdown)	1.1 — 1.3	1.1 — 1.3
Dilution water (m^3)	0.225	0.075

Maintenance

Sulphur-burning plants

Maintenance cost is not directly proportional to output but little error will be introduced if the maintenance cost including manpower is taken as 10 per cent of the battery limit cost. This gives the following figures, rounded off to the nearest 6d.

Output of H_2SO_4 (tons/year)	*Maintenance (shillings/ton of H_2SO_4)*
52,500	11/6
105,000	9/6
210,000	8/—

Pyrites plants

Maintenance costs at the three outputs should be taken as 9 per cent, 10.5 per cent and 12 per cent of the battery limit cost, giving these figures, rounded off to the nearest 6d.

Output of H_2SO_4 (tons/year)	*Maintenance (shillings/ton of H_2SO_4)*
51,000	24/6
102,000	22/6
204,000	20/6

Process labour

Sulphur-burning plants

One process worker per shift would be required in a developed country at each of the three outputs, plus one man on days for sulphur handling. A foreman will be needed if the plant operates on its own, otherwise an existing foreman might supervise the plant as part of his duties. Assuming that the part-time services of a foreman will be available, the process manpower requirements are as follows:

Output of H_2SO_4 (tons/year)	*Man-hours/ton of H_2SO_4*
52,500	0.21
105,000	0.10
210,000	0.05

Pyrites plants

In a developed country, four shift process workers would be needed for each plant. In addition, one plant manager, one foreman and two men for pyrites and cinders handling will be needed, all on days, with a third man on days for the highest output. The process manpower requirements are as follows:

Output of H_2SO_4 (tons/year)	*Man-hours/ton of H_2SO_4*
51,000	0.86
102,000	0.43
204,000	0.23

The man-hours required in a developing country will depend on the skill of the workers available and on the extent to which the plant is mechanized.

Depreciation

This should be taken as 10 per cent of the battery limit cost.

Sulphur-burning plants

Out[illegible]SO_4 ([illegible]	*Depreciation (£/ton of H_2SO_4)*
[illegible]00	0.57
105,000	0.48
210,000	0.40

Pyrites plants

Output of H_2SO_4 (tons/year)	*Depreciation (£/ton of H_2SO_4)*
51,000	1.37
102,000	1.08
204,000	0.86

Pyrites cinders

About half a ton of pyrites cinders is produced for each ton of H_2SO_4 made. The appropriate credit must be allowed.

Overhead costs

A figure must be included to cover this item. A provisional and approximate method for preliminary evaluation has been suggested in section I of chapter 1.

Interest payments

Return on equity capital

These charges have been discussed in section I of chapter 1. The appropriate figures are included here.

Summary

Requirements for production of one ton of H_2SO_4.

	Sulphur burning	*Pyrites*
Sulphur	0.345 tons	
Pyrites		0.75 tons
Steam—credit[a]	0.8 — 1.0 tonnes	1.0 — 1.2 tonnes
Electricity[a]	35 — 50 kWh	60 — 100 kWh
Cooling water	9 — 18 m^3	27 — 72 m^3
Boiler feed water	1.1 — 1.3 m^3	1.1 — 1.3 m^3
Dilution water	0.225 m^3	0.075 m^3
Maintenance[b]	8s to 11s 6d	20s 6d to 24s 6d
Process labour[b]	0.05 — 0.21 man-hours	0.23 — 0.86 man-hours
Depreciation[b]	£0.40 — 0.57	£0.86 — 1.37
Pyrites cinders		credit for 0.5 ton
Overhead charges	to be added	to be added
Interest payments		
Return on equity capital . .		

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[a] Depend on use made of available energy in steam.

[b] Depend on output.

(A preliminary estimate of the total cost can be made from the data given above when unit costs and other factors are known).

F. RAW MATERIAL AVAILABILITY

The plant descriptions in section C, the capital cost estimates in section D and the operating cost estimates in section F of this chapter combine to emphasize the attractiveness of elemental sulphur as a source of SO_2 for sulphuric acid manufacture, ignoring for the moment its availability and price. A sulphur-burning sulphuric acid plant is simple, easy to operate, requires the minimum of labour and needs a lower capital investment than plants that make sulphuric acid from other raw materials. Unfortunately, the position is complicated by doubts about the availability of elemental sulphur in steadily increasing quantities for sulphuric acid manufacture. The medium-term requirements for total sulphur and the availability of elemental sulphur and of pyrites are therefore briefly considered in the following sections.

World sulphur requirements[3]

Market-economy countries consumed 27.7 million tonnes of sulphur in 1968, well over twice their consumption in 1950 and 46 per cent more than in 1962. The 1968 consumption was supplied by 16.7 million tonnes elemental sulphur and 11.0 million tonnes sulphur in other forms, chiefly pyrites, which in 1968 provided almost 60 per cent of the non-elemental sulphur. In the United States and Mexico the Frasch process, described below, produced 9.2 million tonnes elemental sulphur in 1968, while 7.0 million tonnes were recovered from natural and refinery gases and 0.54 million tonnes produced as native refined sulphur in market economy countries. In addition, 1.3 million tonnes elemental sulphur were produced in Poland in 1968 and more than half of this was exported to market-economy countries. In 1966 about 87 per cent of the total sulphur used was converted into sulphuric acid and more than half of this sulphuric acid was used for fertilizer manufacture.

Requirement figures for countries with centrally planned economies are not available but it has been estimated that total world sulphur requirements will exceed 200 million short tons by the end of the century. The ability of elemental sulphur and/or pyrites to meet this great increase in requirement must now be considered.

Production, availability and price of elemental sulphur

Elemental sulphur occurs in a few localities in underground domes, often in areas where oil is produced. The sulphur is recovered by the Frasch process in which sulphur in the dome is melted by superheated water and the molten sulphur raised to the surface by compressed air. Sulphur domes were originally discovered and worked in southern areas of the United States. These domes were for many years the major source of elemental sulphur but by the early 1950s, their output was inadequate to meet rising demands. The result was a sulphur shortage which led in the United Kingdom to increased production of sulphuric acid from indigenous anhydrite. This shortage of elemental sulphur was relieved by the discovery of new sulphur domes chiefly in the Gulf of Mexico and by the recovery of sulphur from natural gas. By the early 1960s, sulphur supplies had overtaken demand and the price of elemental sulphur fell to a low level, with the inevitable effect on production. This in turn led to another sulphur shortage with a consequent sharp increase in sulphur price. This boosted output but, despite large increases in Frasch and recovered sulphur, production did not overtake demand until the middle of 1968.

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[3] SOURCE: *Sulphur* (1968, 1969) Nos. 74, 78, 79, 80 and 81; *Engineering and Mining Journal* (1968) May issue.

In addition to the start-up of new Frasch mines in the United States, a considerable factor in helping supply to overtake demand has been the emergence of Poland as a major supplier of elemental sulphur. Polish sulphur is recovered partly by open-cast mining but the greater part comes from modified Frasch operation in sulphur-bearing limestones.[4]

The end of the sulphur shortage has caused sulphur prices to ease and delivered prices of United States Frasch sulphur in Western Europe at the beginning of 1969 were $2 lower than the year previous. Larger reductions have been made elsewhere. The pattern of world prices for early 1969 below[5] shows a narrowing in the price range as well as a reduction in prices from those for the beginning of 1968.

	$ per ton, cost and freight
North West Europe	45 — 50
Northern Europe	44 — 48
Mediterranean	46 — 50
Latin America	48 — 52
South East Asia/Far East	47 — 53

It is most unlikely that the supply of elemental sulphur will outstrip demand to such an extent that prices will fall to anything like the low levels of the early 1960s, but price reductions may well continue for a few years to bring the price of elemental sulphur appreciably below the early 1969 price.

Can elemental sulphur production be increased substantially or must sulphur users turn increasingly to other forms? Some think that Frasch mining in the United States has reached its zenith and quote as evidence the substantial sums spent on sulphur exploration without finding a major source of exploitable Frasch sulphur. The search for Frasch sulphur in the most likely locations is said to be anything but encouraging and the only bright spot appearing in the Frasch recovery sphere in the United States is in Western Texas (*Engineering and Mining Journal*, 1968). As already stated, substantial sulphur deposits have been found in Poland and are being developed, but their long-term effect on elemental sulphur production cannot yet be assessed.

Elemental sulphur recovered from natural and refinery gases will continue to increase and production from crude oil may some time prove economic. None the less, considered against the background of a continuous increase in total sulphur usage "the industry's failure to identify and start developing major new sources of brimstone supply leaves the medium term situation in doubt . . . Against this background, the wider use of pyrites and of anhydrite/gypsum—both the natural product and of phospho-gypsum—attract and deserve increasing attention as a basis of competitive sulphuric acid supply" (*Sulphur*, 1968, pp. 2—3).

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[4] For description of the Polish sulphur deposits, the mechanism of their formation and the recovery of elemental sulphur see *Sulphur* (1967, 1968) Nos. 72, 77 and 78.

[5] SOURCE: *Sulphur* (1968) No. 79.

The major producers of elemental sulphur (1 million tons per year minimum) are Canada, France, Mexico, Poland, the United States and the Union of Soviet Socialist Republics.

Production, availability and price of pyrites

Pyrites deposits are widespread throughout the world and the Engineering and Mining Journal lists 20 countries that produced more than 100,000 tons in 1966. The largest producers (more than 500,000 tons in 1966) are China (mainland), Cyprus, Finland, Italy, Norway, Portugal, Spain, the United States and the Union of Soviet Socialist Republics. Pyrites deposits are not only widely disseminated, but extensive. Sulphur in the form of pyrites is available to meet increasing sulphuric acid demands for many years.

Pyrites have long been used to make SO_2 for sulphuric acid manufacture, but a plant for making sulphuric acid from pyrites is more complex than that for making sulphuric acid from elemental sulphur. The unit price of sulphur in pyrites[6], while related to that of elemental sulphur, has always been lower to make pyrites a competitive raw material for sulphuric acid manufacture.

The prices of pyrites produced in Europe are based on the price of pyrites from the very large Spanish deposits. At the beginning of 1969 the price of Spanish pyrites, f. o. b. at the port of Huelva, was £4.65 per ton of material containing 48 per cent S, equivalent to £9.7 per ton of sulphur (*Sulphur*, 1968, p. 2). With the addition of freight charges, (1 ton of pyrites contains only 0.5 ton of sulphur), this price is less than the cost of elemental sulphur and makes it essential to consider pyrites as a raw material for sulphuric acid manufacture in new plants in locations where pyrites cinders can be disposed of at a reasonable price.

Summary

World requirements for sulphur in all forms is expected to increase at a considerable rate in the remainder of the century. There are doubts about the ability of elemental sulphur to meet these rapidly increasing demands. Ample pyrites supplies are available and the manufacture of sulphuric acid from pyrites is a well established process. Ample supplies of calcium sulphate are also available and its use in sulphuric acid manufacture is discussed in the following chapter. Serious consideration should be given to pyrites as an alternative to elemental sulphur for new sulphuric acid production.

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[6] One unit of sulphur = $\frac{1}{100}$ of a ton.

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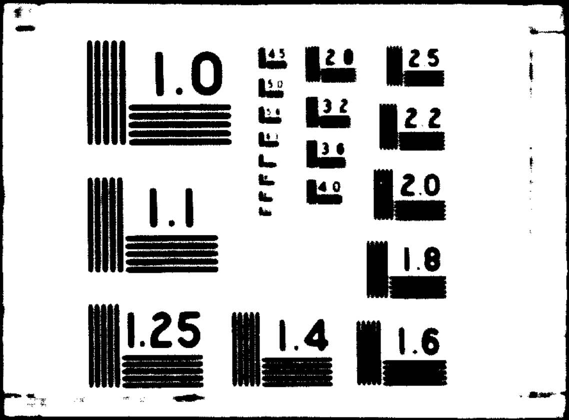

3. PORTLAND CEMENT FROM MINERAL CALCIUM SULPHATE

A. REPLACEMENT OF LIMESTONE BY CALCIUM SULPHATE

The process for the manufacture of ordinary Portland cement clinker has been described in section G of chapter 1. Calcium carbonate in the forms of limestone and chalk is decomposed by heat into lime with evolution of carbon dioxide

$$CaCO_3 = CaO + CO_2.$$

The decomposition pressure reaches 1 atm at about 900° C. The lime produced combines with silica, alumina and ferric oxide to form cement clinker.

The analagous reaction with a sulphur-bearing calcium compound would be the thermal decomposition of calcium sulphite

$$CaSO_3 = CaO + SO_2.$$

Unfortunately calcium sulphite is an unstable substance which does not occur naturally. The most closely related compound that does occur in large deposits is calcium sulphate, found as anhydrite ($CaSO_4$) and gypsum ($CaSO_4\,2\,H_2O$). On heating, gypsum loses water at a relatively low temperature to form anhydrite. Hence if gypsum is used in a kiln process, anhydrite is the material from which lime has ultimately to be produced to combine with SiO_2, Al_2O_3 and Fe_2O_3 to make cement clinker with simultaneous formation of SO_2 for sulphuric acid manufacture. Possible methods of producing lime from anhydrite are considered below.

Thermal decomposition of anhydrite

Anhydrite decomposes on heating much less readily than limestone to give lime, sulphur dioxide and oxygen

$$CaSO_4 = CaO + SO_2 + \tfrac{1}{2}\,O_2.$$

Hofman and Mostowitsch (1909) studied the decomposition of synthetic calcium sulphate (gypsum heated to constant weight at 1,150° C) in a stream of purified dry air. Decomposition began at about 1,200° C and increased with temperature to give a weight loss of 30 — 40 per cent after 10 minutes at 1,400° C with fusion of the material. The decomposition pressures above calcium sulphate were studied by Marchal (1926) and Zawadzki (1932). Zawadzki found that the total gas pressure above natural anhydrite was 2.4 mm Hg at 1,180° C rising to 31.2 mm Hg at 1,340° C and to 47.5 mm Hg at 1,370° C. The total gas pressure is plotted against temperature in figure 8.

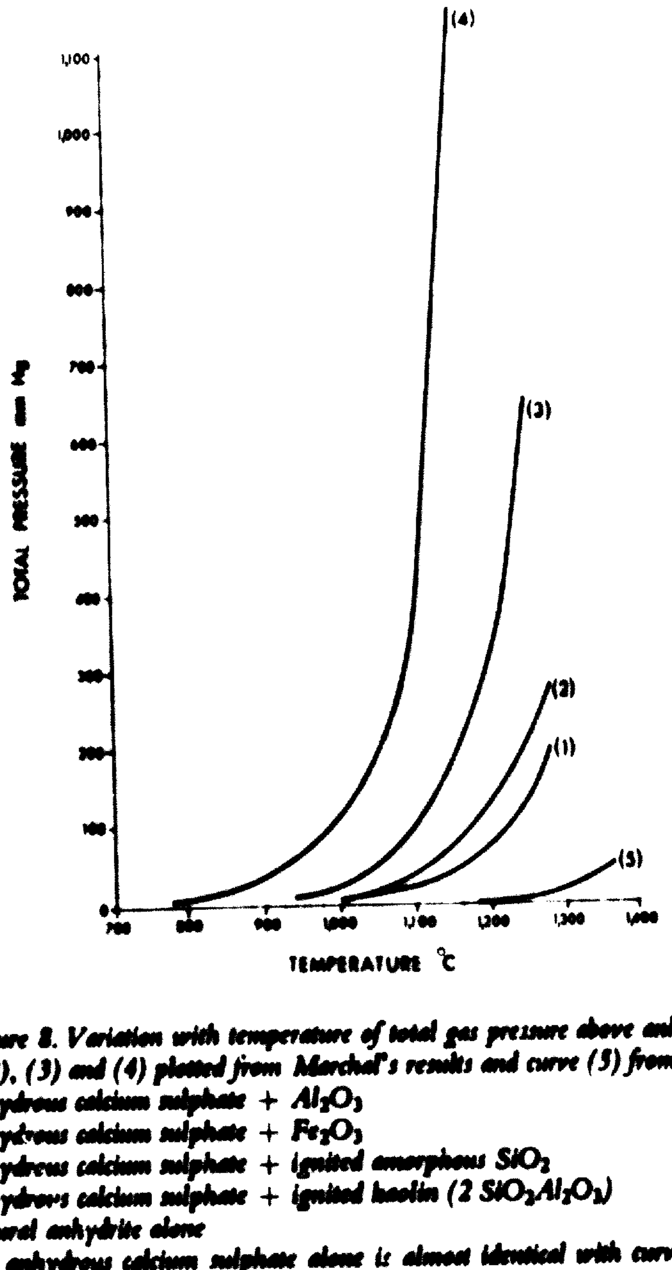

Figure 8. Variation with temperature of total gas pressure above anhydrite
Curves (1), (2), (3) and (4) plotted from Marchal's results and curve (5) from Zawadzki's results
Curve (1) anhydrous calcium sulphate + Al_2O_3
Curve (2) anhydrous calcium sulphate + Fe_2O_3
Curve (3) anhydrous calcium sulphate + *ignited amorphous* SiO_2
Curve (4) anhydrous calcium sulphate + *ignited kaolin* ($2\,SiO_2Al_2O_3$)
Curve (5) natural anhydrite alone
The curve for anhydrous calcium sulphate alone is almost identical with curve (1) and cannot be differentiated from it sufficiently to be shown here.
Anhydrous calcium sulphate in curves (1) to (4) was obtained by dehydration of gypsum.

The free energy for the decomposition of anhydrite calculated from Zawadzki's results can be expressed as $\Delta F^{\circ} = 118{,}000 - 60.5\,T$ from which $\Delta F^{\circ} = 0$ at 1,680° C. Hence the equilibrium moves in favour of the production of $SO_2 + \frac{1}{2}\,O_2$ above 1,680° C. Clearly the thermal decomposition of anhydrite is not a suitable reaction for the production of lime in a kiln where the normal clinkering temperature is about 1,450° C. Operation at higher temperatures would involve molten anhydrite with a high heat requirement and pose very difficult chemical engineering problems. Most of the published work on the decomposition of calcium sulphate was done on pure calcium sulphate obtained by the ignition of synthetic gypsum. It is not always easy to be sure of the exact state of the calcium sulphate used but it is of interest to note that some samples of dehydrated gypsum had a considerably higher decomposition pressure than natural anhydrite (Marchal, 1926; Zawadzki, 1932). This is shown in figure 8 where curve (1) can be regarded as the decomposition pressure above dehydrated gypsum. The decomposition pressure of dehydrated gypsum falls with time and temperature of heating and ultimately approaches that of anhydrite. Zawadzki was of the opinion that anhydrous calcium sulphate existed in at least two forms which he called dehydrated gypsum and anhydrite. Dehydrated gypsum changes fairly rapidly at 1,200° C into anhydrite. The transformation temperature is at a lower but unknown temperature. Zawadzki considered that his earlier pressure measurements and those of Marchal corresponded to a system undergoing transformation and, not having reached equilibrium, are much higher than the true anhydrite decomposition pressures.

Thermal decomposition of anhydrite in the presence of SiO_2, Al_2O_3 and Fe_2O_3

In practice, the production of cement clinker from anhydrite would require it to be heated with SiO_2, Al_2O_3 and Fe_2O_3. The behaviour of anhydrite when heated in the presence of these substances must therefore be considered. Hofman and Mostowitsch showed that the temperature at which decomposition began was reduced by SiO_2 to 1,000° C and by Fe_2O_3 to 1,100° C and the amount of decomposition increased. This is due to the entry of the CaO formed by thermal decomposition into other equilibria with SiO_2 and Fe_2O_3 to form calcium silicates and ferrites.

The total gas pressures above mixtures of dehydrated gypsum with kaolin ($2 SiO_2Al_2O_3$), SiO_2, Al_2O_3 and Fe_2O_3 were measured by Marchal. Her results are shown graphically in figure 8, from which it can be seen that the total gas pressure is increased appreciably by Fe_2O_3, considerably by SiO_2 and very much by kaolin. The curve for dehydrated gypsum alone is almost identical with that for dehydrated gypsum with Al_2O_3. The reason for the very large increases obtained with kaolin is not known. They are possibly the result of the system not having reached equilibrium.

Corresponding measurements with anhydrite are not available, but as explained above the pressures would be expected to be considerably lower. The curves therefore exaggerate the effect of these additions on the thermal decomposition of anhydrite. It must also be remembered that the SiO_2 used was an ignited gel which would be expected to be much more reactive than sand, which is the cheap form of SiO_2 normally used in industry. It would therefore be expected that the decomposition pressures of mixtures of anhydrite with these additives would not reach 760 mm Hg at a temperature below the fusion point of anhydrite. Hence the thermal decomposition of anhydrite in the presence of SiO_2, Al_2O_3 and Fe_2O_3 will not provide the CaO needed for the production of cement clinker by a method that is industrially acceptable.

A variety of compounds can be formed by heating anhydrite with SiO_2, Al_2O_3 and Fe_2O_3. The free energies of formation of these compounds are not all known but approximate free energy equations for the various reactions can be calculated. These show that the effectiveness of the additives in increasing the total gas pressure is $SiO_2 > Fe_2O_3 > Al_2O_3$, which agrees with the experimental results (cf. Dijksman, 1958, p. 333).

Reduction of calcium sulphate

The reduction of calcium sulphate was examined many years ago to ascertain if this offered a method of recovering sulphur from calcium sulphate. The reduction of calcium sulphate with carbon or carbon monoxide commences at

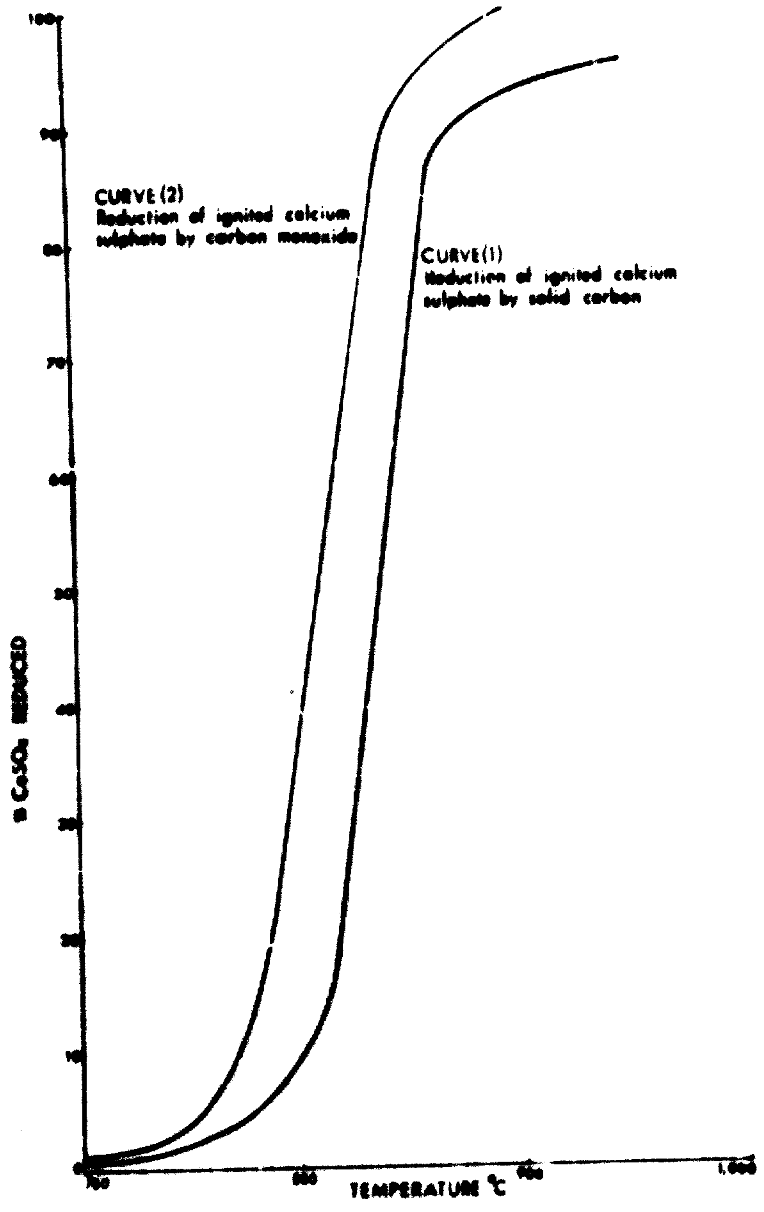

Figure 9. Variation with temperature of reduction of calcium sulphate

a much lower temperature than thermal decomposition and goes readily to completion. Reaction with carbon takes place according to the equation:

$$CaSO_4 + 2\,C = CaS + 2\,CO_2.$$

This reaction and the reduction of calcium sulphate by carbon monoxide were studied by Hofman and Mostowitsch (1911). The decomposition curves they obtained with carbon and carbon monoxide are shown in figure 9. It will be seen that reduction of calcium sulphate by carbon was detectable at 700° C, rapid between 800° C and 900° C, and complete below 1,000° C. With coke, reduction is said to commence at 900° C and continue to 1,100° C (Hull, Schon and Zirngibl, 1957).

The free energy of the reaction $CaSO_4 + 2\,C = CaS + 2\,CO_2$ can be expressed by the equation $\Delta F^\circ = 38{,}375 - 81.59\,T$, from which it may be calculated that $\Delta F^\circ = 0$ at 200° C. This reaction is therefore thermodynamically capable of producing calcium sulphide at relatively low temperatures, the limitation being the speed at which the reaction occurs. The kinetics of the reduction of calcium sulphate with both solid and gaseous reducing agents has been discussed by Dijksman. The rate of reaction in both cases is a function of temperature, the concentration of reducing agent, the ratio of concentration of reducing agent to that of calcium sulphate and to the total surface area of the calcium sulphate.

With solid reducing agents such as coal, coke or carbon, reduction of calcium sulphate is preceded by gasification of the reducing agent. The velocity of the forward reaction is independent of the particle size of the reducing agent within wide limits but increases with decrease in the size of $CaSO_4$ particles. Dijksman's results indicate that at high temperature (> 800° C) the kinetics of the reaction with gaseous reducing agents are controlled by the rate of diffusion of the reducing gas to the surface of the calcium sulphate. Reduction with coke will therefore be controlled by the diffusion of the reducing gas formed from coke.

The reduction of calcium sulphate produces calcium sulphide and not calcium oxide as required for clinker production. Further, the calcium sulphide produced contains all the sulphur present in the original calcium sulphate. Hofman and Mostowitsch therefore examined the behaviour of calcium sulphide when heated in a stream of purified dry air to determine if the sulphur in it could be released as SO_2. They found that about two thirds of the calcium sulphide was re-oxidized to calcium sulphate but that one third of the sulphur initially present in calcium sulphide was lost as SO_2 produced according to the equation

$$3\,CaSO_4 + CaS = 4\,CaO + 4\,SO_2.$$

This reaction, under their particular experimental conditions, began at about 800° C and became rapid between 850° and 900° C. It will be seen that this reaction offers the possibility of producing CaO for clinker formation at an acceptable temperature but the simultaneous formation of large quantities of calcium sulphate showed that, in the presence of sufficient oxygen, the oxidation of calcium sulphide proceeded more rapidly than the interaction of calcium sulphide and calcium sulphate. This was confirmed by Neumann (1926) who also showed that the reaction between calcium sulphide and calcium sulphate could be carried to completion at 1,000° C in a stream of pure nitrogen.

The system $CaSO_4$—CaS is so fundamental to the production of cement and SO_2 from anhydrite that it must be considered in more detail.

The system $CaSO_4$—CaS

This system was studied by Zawadzki (1932 and 1925...1930) as part of his investigation of the system calcium-sulphur-oxygen and by Schenck and his co-workers (1929, 1933). Zawadzki summarized his results in these equations:

$$CaS + 3\,CaSO_4 \rightleftarrows 4\,CaO + 4\,SO_2 \qquad (a)$$

$$CaS + 2\,SO_2 \rightleftarrows CaSO_4 + S_2 \qquad (b)$$

$$4\,CaO + 6\,SO_2 \rightleftarrows 4\,CaSO_4 + S_2 \qquad (c)$$

Reaction (c) need not be taken into account because it must be in equilibrium if reactions (a) and (b) are in equilibrium. The partial pressure of SO_2 in the system is governed by the reaction $3\,CaSO_4 + CaS = 4\,CaO + 4\,SO_2$ and the ratio $p\,S_2/p\,SO_2$ by the reaction $CaS + 2\,SO_2 = CaSO_4 + S_2$.

Zawadzki's data lead to the following equation for the free energy of reaction (a). $\Delta F^\circ = 225{,}000 - 153\,T$, whereas Schenck's give $\Delta F^\circ = 102{,}000 - 59.6\,T$. ΔF° becomes zero at 1,200° C (Zawadzki) and 1,440° C (Schenck). Dijksman says that Zawadzki's equation is reasonably close to that which can be derived from other equilibria but also states that an equation derived from a combination of several equilibria cannot be of first-class accuracy. Dijksman therefore redetermined the total equilibrium pressure of $SO_2 + S_2$ over the system $CaS + 3\,CaSO_4$. His results give a free energy equation $\Delta F^\circ = 219{,}500 - 150\,T$ whence ΔF° becomes zero at about 1,190° C. This is in good agreement with Zawadzki's result and indicates that the decomposition pressure becomes 1 atm at about 1,200° C. Figure 10 summarizes the information on the free energies of this reaction and shows that Schenck's results must be erroneous. Figure 10 also shows that the forward reaction giving CaO and SO_2 is favoured by increase in temperature.

It is clearly important to know the influence of SiO_2, Al_2O_3 and Fe_2O_3 on this equilibrium. Neumann found that the reaction of CaS and $3\,CaSO_4$ at 900° C in a stream of nitrogen was increased from 17 per cent to 66 per cent by the addition of siliceous blast furnace slag. Dijksman states that the influence of SiO_2, Al_2O_3 and Fe_2O_3 on the equilibrium can be calculated approximately from free energy data. The thermodynamic data do not permit precise calculations to be made but the addition of SiO_2 and Fe_2O_3 could be expected to result in a pressure of 1 atm being reached at about 870° and 1,100° C respectively, whereas Al_2O_3 addition should have little effect. Dijksman measured the equilibrium pressures over the system $CaS + 3\,CaSO_4$ with the addition of SiO_2, Al_2O_3, and Fe_2O_3 respectively. The experimental results are given in figure 11

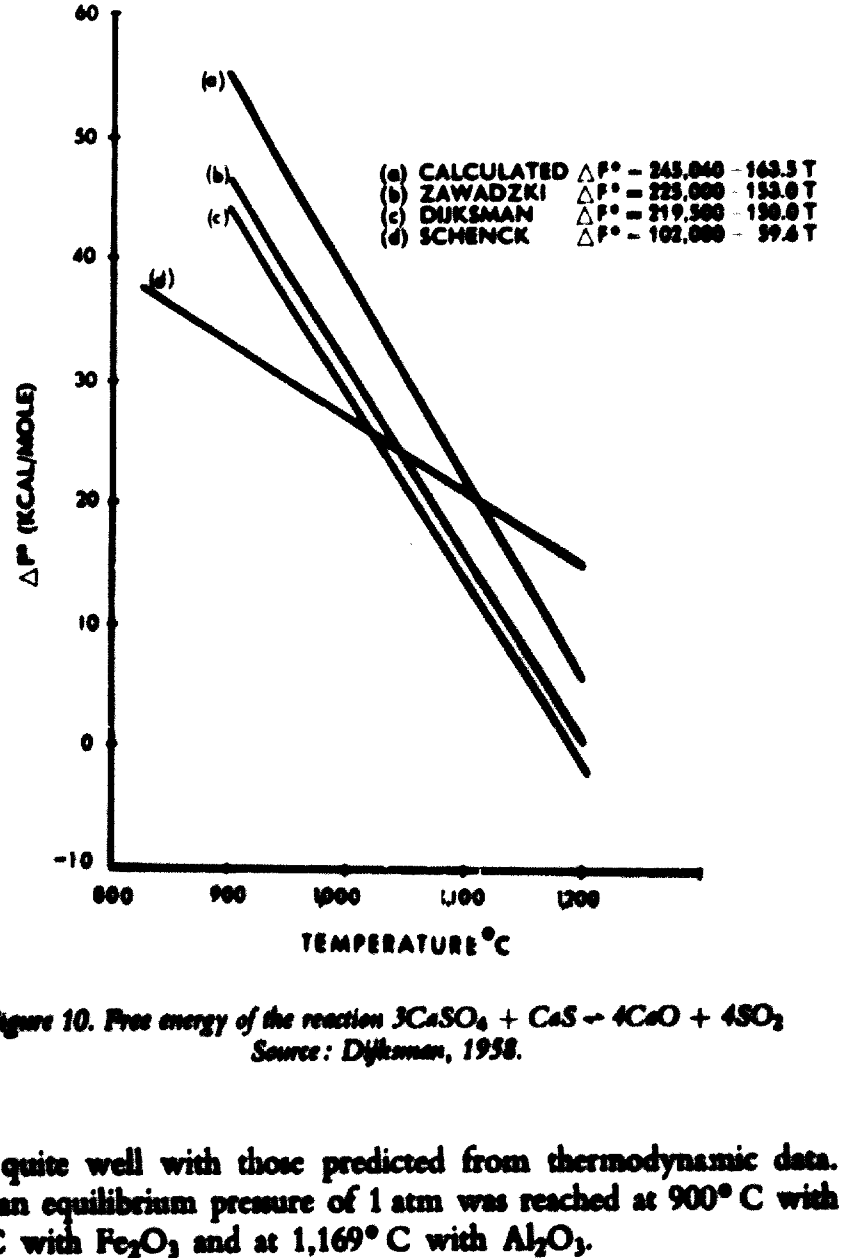

Figure 10. Free energy of the reaction $3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$
Source: Dijksman, 1958.

and agree quite well with those predicted from thermodynamic data. They show that an equilibrium pressure of 1 atm was reached at 900° C with SiO_2, at 1,078° C with Fe_2O_3 and at 1,169° C with Al_2O_3.

The reaction between $CaS + 3\ CaSO_4$ in the presence of SiO_2, Al_2O_3 and Fe_2O_3 thus provides the basis of a practicable method of producing Portland cement and SO_2 from anhydrite. It is therefore important to consider the mechanism and kinetics of the reaction $CaS + 3\ CaSO_4$.

Dijksman points out that two possible mechanisms for the reaction can be postulated:

(a) The reaction proceeds through the gas phase as in the reduction of $CaSO_4$ with carbon;

(b) The reaction is a solid-solid interaction.

Solid CaS and $CaSO_4$ heated together in the same reaction vessel but without actual physical contact showed no evidence of reaction. This favours *(b)* as the mechanism of the reaction. Supporting evidence is provided by the rate of the reaction. If the reaction proceeded through the gas phase, the initial step would

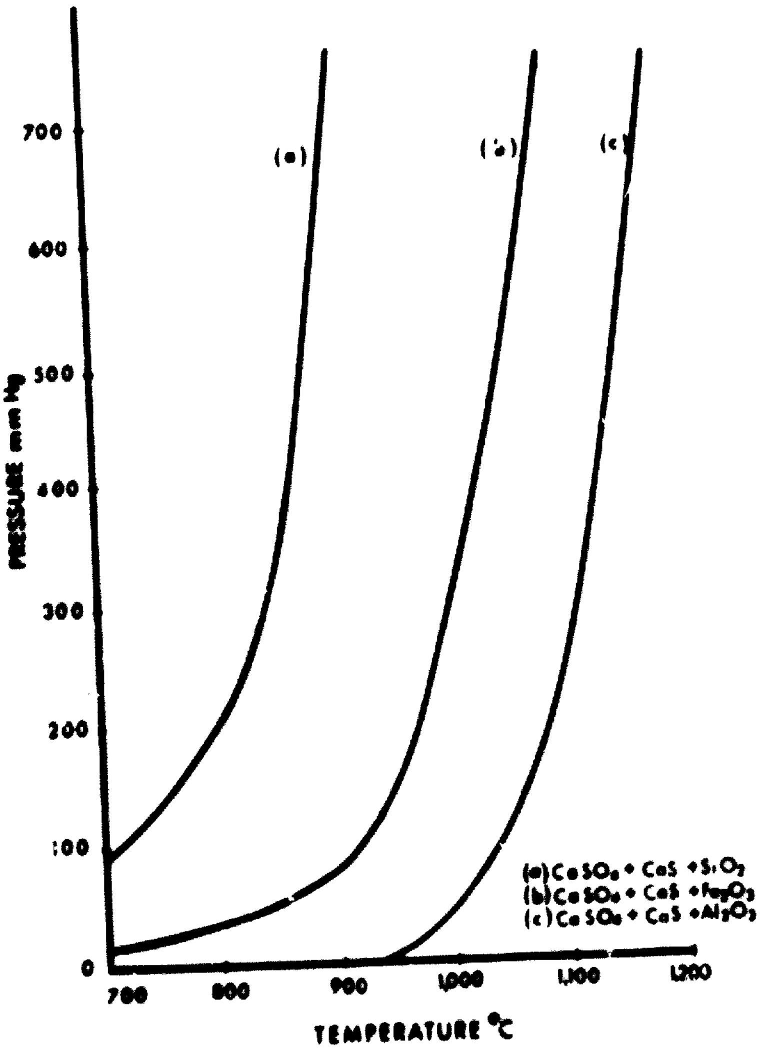

Figure 11. Influence of acidic oxides on reaction $3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$
Source: Dijksman, 1958.

be the decomposition of $CaSO_4$, since CaS is thermally stable in a neutral atmosphere to very high temperatures and the reaction rate of CaS and 3 $CaSO_4$ would be controlled by the rate of decomposition of $CaSO_4$. This is obviously not the case because the rate of reaction between CaS and 3 $CaSO_4$ is very much greater than the rate of thermal decomposition of $CaSO_4$ alone.

There is considerable evidence that the reaction is in fact a solid-solid interaction. Thus, the reaction is very temperature dependent and therefore has a high activation energy. This agrees with the concept of a solid-solid reaction because if the rate controlling factor were gas diffusion, the activation energy would be small. Dijksman found that when a cube of anhydrite was heated with one face resting on a layer of powdered CaS, reaction between the anhydrite and CaS occurred only where there was physical contact between them.

Dijksman refers to the work of Jander (1927) and Jagitsch and Hedvall (1944), who investigated solid-solid reactions involving gas evolution. These authors described two types of solid-solid reactions: for one the reaction rate is controlled by the chemical reaction at the interfaces of the reactants and is therefore independent of the thickness of the product layer; for the other the reaction rate is controlled by diffusion of one or both reactants through the product layer.

Dijksman's experimental work led to the conclusion that the reaction between CaS and $3\,CaSO_4$ was controlled by diffusion, except for the first few minutes of the reaction. This is probably because the diffusion mechanism does not control the reaction rate before an appreciable product layer has been formed.

Reaction in Dijksman's determination of reaction equilibria began at temperatures over 900° C and equilibrium at a given temperature was reached comparatively rapidly. Hull, Schon and Zirngibl (1957) state that the addition of clay or similar material to $CaS + 3\,CaSO_4$ produced quantitative decomposition in one hour at 1,100° C.

One conclusion to be drawn from the fact that the interaction of CaS and $CaSO_4$ is a solid-solid reaction controlled by diffusion is that the anhydrite in a kiln (which also produces the CaS) must be finely divided. As stated in this section diminution in anhydrite particle size also assists its reduction. Another conclusion to be made from the work of Hofman and Mostowitsch is that the amount of oxygen present when CaS and $CaSO_4$ react must be carefully controlled to avoid the re-oxidation of CaS to $CaSO_4$.

It is now necessary to consider the reaction $CaS + 2\,SO_2 = CaSO_4 + S_2$ because this reaction controls the ratio S_2/SO_2 in the gas at equilibrium and the presence of appreciable amounts of elemental sulphur in the kiln exit gas would cause serious operating difficulties in the purification of the kiln gas. Dijksman determined the ratio of S_2/SO_2 in the gas over the system $CaS + 3\,CaSO_4$ at various temperatures and from these calculated the free energy of the reaction $CaS + 2\,SO_2 = CaSO_4 + S_2$. This is plotted against temperature in figure 12 which also shows the equations derived from the measurements of Schenck and Zawadzki. It will be seen that Schenck's equilibria for the reaction, the calculated equilibria and those obtained by Dijksman agree reasonably well, but Zawadzki's results are outside the limits of accuracy of the calculated equation.

It may therefore be concluded that $\Delta F^\circ = 0$ at about 900° C when

$$\frac{p\,S_2}{p\,SO_2} = 1.$$

The effect of temperature and pressure on the S_2/total S ratio in the reaction $CaS + 2\,SO_2 \rightleftharpoons CaSO_4 + S_2$ is shown in figure 13. It will be seen that there is a sharp fall in the S_2/total S ratio with increase in temperature. This ratio also falls with decrease in the total pressure $S_2 + SO_2$.

In conformity with this, Fleck reported that the amount of elemental sulphur produced from a mixture of $CaSO_4$, C, SiO_2, Al_2O_3 and Fe_2O_3 under specified reaction conditions increased from 15 per cent with coke to 30 per cent

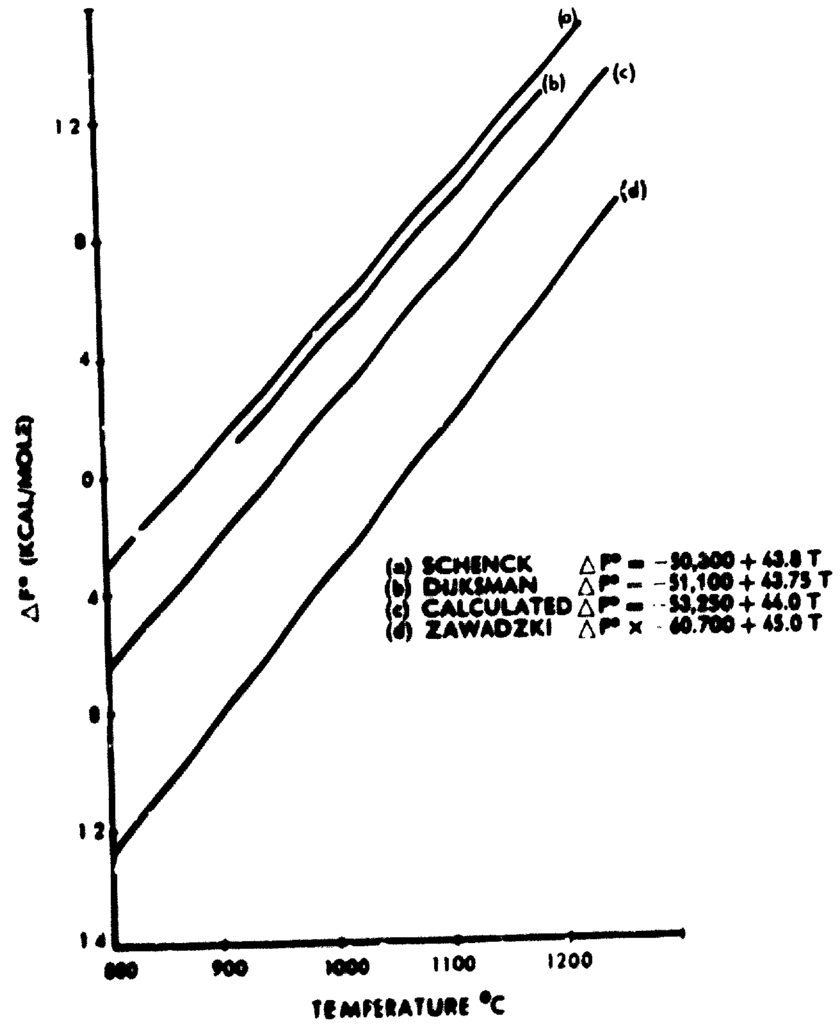

Figure 12. Free energy of the reaction $CaS + 2SO_2 \rightarrow CaSO_4 + S_2$
Source: Dijksman, 1955.

with charcoal and to 50 per cent with coal. Coal is active as a reducing agent at a lower temperature than coke. The reduction of $CaSO_4$ to CaS will therefore proceed at a lower temperature with coal than with coke and the equilibrium between SO_2 and S_2 over CaS will be established at this lower temperature with consequent increase in the proportion of sulphur present.

Dijksman calculated the heat of reaction from this free energy data and obtained a value $H_{298} = -58.48$ kcal/g mole, which is in good agreement with the figure of -55.35 kcal/g mole obtained from standard thermodynamic data.

Dijksman also made a preliminary study of the kinetics of the oxidation of CaS with SO_2 and showed that the rate of reaction is dependent on temperature and on the ratio of concentration of SO_2 to that of CaS. The value of the velocity constant for this oxidation reaction increases rapidly with temperature to a maximum at about 800° C and then falls smoothly to approach a value of zero at 1,000° C.

These thermodynamic and kinetic data can be used to show that very little elemental sulphur can be derived from the reaction of CaS and SO_2 in

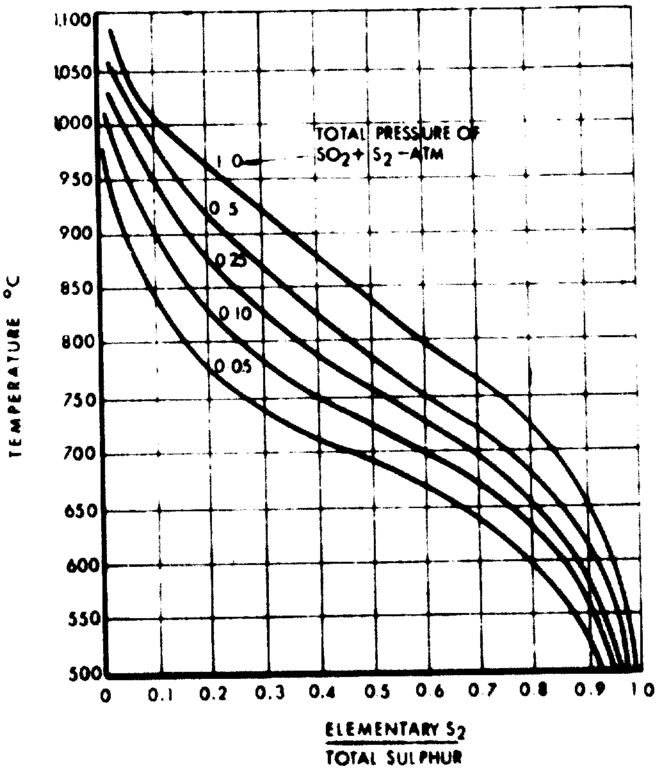

Figure 13. Effect of temperature and pressure
Source: Fleck, 1952.

an anhydrite kiln and that the sulphur content of the gas leaving a correctly controlled anhydrite kiln is very low. As already stated, the reduction of $CaSO_4$ to CaS by coke begins in the kiln at 900° C and continues to 1,100° C. Interaction of CaS and $CaSO_4$ occurs in the same temperature range in the presence of SiO_2, Al_2O_3 and Fe_2O_3 and therefore the production of SO_2 does not begin until the kiln burden reaches a temperature of 900° C. The combustion gases, mostly N_2 and CO_2, pass rapidly through the kiln countercurrent to the solid flow and become charged with SO_2 from the kiln burden. The reaction velocity for the reaction $CaS + SO_2 \rightarrow CaSO_4 + S_2$ is zero at 1,000° C so that this forward reaction can only occur for a short period in the kiln (900° to 1,100° C) where its velocity will be relatively low. The contents of the kiln will not have reached equilibrium at 900° C and the sulphur content of the gas will be lower than corresponds to equilibrium at that temperature. If the contents of the kiln were in equilibrium at 900° C, in particular if the system $CaS + SO_2 = CaSO_4 + S_2$ were in equilibrium at 900° C where $\Delta F^\circ = 0$, it can be shown that

$$\frac{p\,(S_2)}{p\,(SO_2)^2} = 1, \text{ whence } p\,(S_2) = p\,(SO_2)^2.$$

The sulphur content of kiln gas containing 8 — 9 per cent of SO_2 in equilibrium at 900° C would therefore be 0.64 — 0.81 per cent. The actual sulphur content will be much less and, given a small excess of air, will be oxidized to SO_2. This is discussed later in section B of this chapter.

It must be realized, however, that elemental sulphur can be formed in undesirable amounts during the interaction of $CaSO_4$, C, SiO_2, Al_2O_3 and Fe_2O_3 in a kiln if this interaction is carried out in a reducing atmosphere. It is not necessary to discuss the precise mechanisms by which sulphur can be produced. It is sufficient to emphasize the importance of maintaining the correct conditions in the kiln, avoiding alike the reducing conditions that produce elemental sulphur and the oxidizing conditions that reconvert CaS to $CaSO_4$.

B. PRODUCTION OF PORTLAND CEMENT AND SO_2-CONTAINING GAS FROM CALCIUM SULPHATE

Process

It is now possible to state in general terms a process for the production of Portland cement clinker and SO_2-containing gas from calcium sulphate. Anhydrite, coke and sources of SiO_2, Al_2O_3 and Fe_2O_3 are ground, mixed and heated to clinkering temperature (1,450° C) in a rotary kiln. The over-all reaction between anhydrite and coke is:

$$2\,CaSO_4 + C = 2\,CaO + 2\,SO_2 + CO_2.$$

The CaO so produced combines with the acidic oxides in the usual way to form Portland cement clinker. In practice, a slightly higher mole ratio $C/CaSO_4$ is used than is indicated by this equation to compensate for the carbon in the raw meal which burns directly to CO_2.

Control of the $C/CaSO_4$ ratio is fundamental to the success of the process. Raw meal with too little carbon will produce material that contains too much $CaSO_4$ when it enters the clinkering zone with the result that there will be too much liquid in this zone. On the other hand, raw meal with too much carbon will give material containing an excess of CaS, which softens at high temperatures causing agglomeration.

Either condition leads to operational difficulties and produces clinker containing appreciable amounts of $CaSO_4$ or CaS. The former might make it difficult not to exceed the permitted SO_3 content in the cement made from such clinker. BS 12 : 1958 does not specify a permitted sulphide content of cement but cement containing more than a fraction of a per cent of CaS turns blue when hydrated. This colour does not affect the strength of the concrete but may cause suspicion that the cement has been adulterated with basic slag. Producers of cement from anhydrite usually have their own limit for CaS content of the cement to avoid complaints from users of the cement.

The other constituents of clinker must be carefully controlled also. High SiO_2 or high Al_2O_3 in raw meal can produce operational difficulties and the ratio $SiO_2/Al_2O_3 + Fe_2O_3$ must be carefully controlled as well as the absolute amounts present. The air entering the kiln must be carefully controlled to avoid production of elemental sulphur or re-oxidation of CaS to $CaSO_4$. This is done by ensuring that conditions are neither oxidizing nor reducing when $CaSO_4$

reduction begins in the kiln. In practice, the kiln exit gas contains a fraction of a per cent of oxygen. Air is blown into the kiln smoke box or part way along the kiln, to ensure that the gas entering the gas purification plant is free from elemental sulphur. It is obviously necessary to reduce all uncontrolled air intakes, for example, through imperfect seals, to a minimum.

The kiln burner has analytical data, air flow and temperature measurements to assist him in the correct operation of the kiln, but this depends to a large extent on his skill and judgement. A skilled kiln burner can tell from the appearance of the kiln whether it is operating correctly or whether the kiln burden is high in $CaSO_4$, CaS, SiO_2 or Al_2O_3, or whether the clinker is overburned or underburned. This skill can only be passed on from a skilled burner to a trainee on a working kiln.

The requirements of production control and the training procedure for personnel to be in charge of production control form part of the know-how of the operators and cannot be further discussed in this report. This know-how also includes kiln design that provides minimum dust formation and accurate retention time, experience in kiln lining that gives maximum performance, and procedures for starting and shutting down kilns.

It will by now be evident that the control of a kiln using anhydrite is more difficult and must be more precise than that of a kiln using limestone. The consequences of mal-operation are also more serious. These difficulties must not be exaggerated because the process is successfully operated at seven locations (see appendix to this chapter), but developing countries considering this process must appreciate that it is technologically a more difficult process than manufacture of clinker from limestone. A larger number of variables must be controlled within narrower limits for satisfactory kiln operation.

Product

Analyses of anhydrite clinkers given in the literature fall within the limits of composition given earlier. Examination by X-ray diffraction of the cement ground from an anhydrite clinker indicated the existence of the normally expected cement compounds. Nothing of an abnormal nature was observed in the diffraction pattern of this sample (*Cement and Lime Manufacture*, 1968). Cement made from anhydrite clinker in the United Kingdom is sold through the Associated Portland Cement Manufacturers—who make Portland cement from calcium carbonate—and fully meets British Standard specifications (Hull, Schon and Zirngibl, 1957). It would be unwise, however, to conclude that clinkers made from limestone and from anhydrite are therefore identical in composition. The effect of minor components such as P_2O_5 and F in Portland cement is discussed later in section B of chapter 4, where it is shown that these components are capable of causing profound structural modifications to C_2S and C_3S and thus play a much more important part in cement quality than the amounts present in the clinker might suggest.

Gutt and Smith (1966) have begun an investigation of high temperature phase equilibria in the system $CaO—SiO_2—SO_3$. They have reported the location of a new compound (2 $CaOSiO_2)_2CaSO_4$ (Gutt and Smith 1966). This formula can be written as 2 $C_2S \cdot CaSO_4$ (cf. 2 $C_2S \cdot C_3P$ in chapter 4, p. 72). Further information is given by Gutt and Smith (1968). The newly detected silico sulphate does not appear to form detectable solid solutions with other phases and it decomposes at 1,298°C ± 2°C. The only solid solution detected was between C_2S and Ca^{2+} and SO_4^{2-} ions. The solubility of Ca^{2+} and SO_4^{2-} ions in α'-form of C_2S is thought to be higher than in β-form of C_2S. The maximum solid solution of α'-form of C_2S with Ca^{2+} and SO_4^{2-} ions at 1,200°C can be represented as 98.9 C_2S : 1.1 $CaSO_4$ mol per cent and at 1,000°C as 98.3 C_2S : 1.7 $CaSO_4$ mol per cent.

Much work remains to be done and firm conclusions on the effect of $CaSO_4$ in anhydrite clinker cannot yet be made but there is the possibility that $CaSO_4$, by entering into solid solution with one of the calcium silicate constituents, may cause structural modifications which affect cement quality. As already stated, Portland cement made from anhydrite meets current quality requirements, but an understanding of the effect of calcium sulphate in anhydrite clinker, if this emerges from the work of Gutt and Smith, may enable anhydrite cement quality to be improved still further.

Production

A simplified line diagram is given in figure 14.

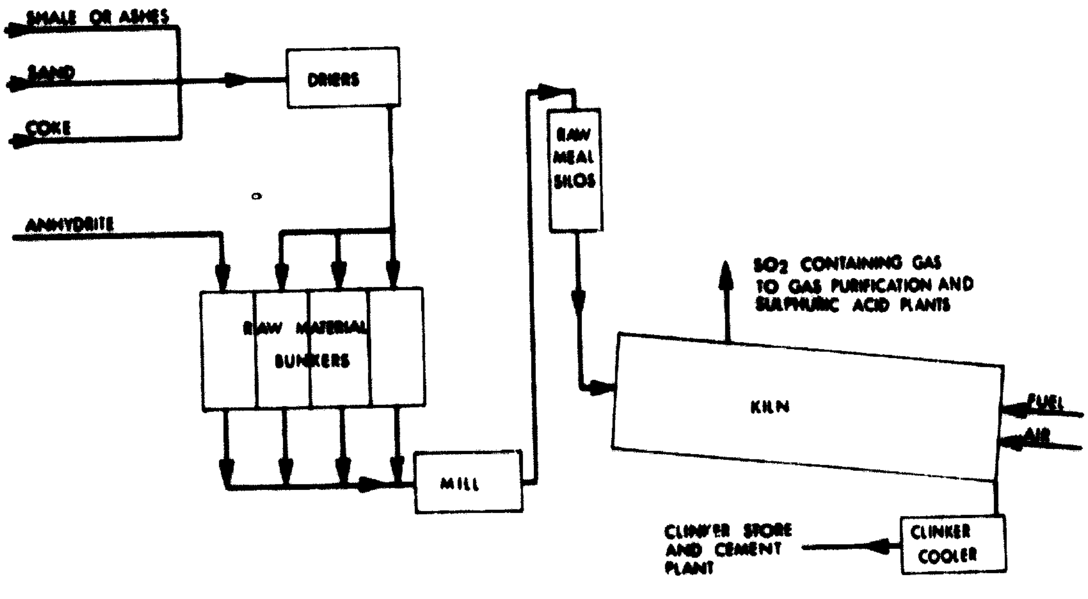

Figure 14. Simplified flowsheet for anhydrite kiln plant

Raw materials

Mineral calcium sulphate in the forms of anhydrite or gypsum can be used as sources of CaO and SO_3. If gypsum were used and fed direct to the kiln in the raw meal, the SO_2 containing gases leaving the kiln would be diluted with the products of combustion ($CO_2 + N_2$) of the extra fuel needed to remove combined water from the gypsum. As will be seen later, this dilution is undesirable. Gypsum is therefore dehydrated to hemihydrate or anhydrite before incorporation in raw meal. Anhydrite is therefore preferred to gypsum as a raw material because of the additional cost of processing gypsum before incorporation in raw meal.

Silica can be supplied as sand or shale (which also contributes Al_2O_3, Fe_2O_3 and some CaO), or a mixture of each. If sand is used as the major source of silica, Al_2O_3 and Fe_2O_3 can be supplied in coal ash from boilers. Pyrites cinders can also be used to supply Fe_2O_3. These raw materials are usually cheap, and their availability determines which of them are used. Any combination of them that gives the required over-all composition and does not introduce too much MgO or alkali metals can be used. Excess of alkali metals can cause difficulty in the gas cleaning system. If the kiln is coal-fired, allowance must be made (as with a limestone kiln) for the SiO_2, Al_2O_3 and Fe_2O_3 introduced by the coal ash into the kiln burden. Carbon is supplied as coke, which also contributes some SiO_2, Al_2O_3 and Fe_2O_3. It is desirable that the composition of the raw materials should vary as little as possible to assist in the production of raw meal of constant composition.

Preparation of raw materials

The raw materials are prepared in a similar way to that described in section F of chapter 1. Anhydrite does not normally need drying although it may require crushing before it is conveyed to its storage bunker. The other raw materials are all dried before being taken to individual dried raw material bunkers. Drying is necessary to prevent variations in moisture content which would affect raw meal composition, and to ensure that the raw materials can be handled and proportioned satisfactorily. The raw materials are weighed into mills, where they are ground and mixed. The raw meal leaving the mills is taken, usually by pneumatic conveyor, to raw meal storage and blending silos, which are interconnected to enable raw meal to be produced of the exact composition required for the kiln. Properly proportioned raw meal is fed to the kiln at a controlled rate either directly or through raw meal feed hoppers. Alternatively, the constituents of raw meal can be dried, ground and stored separately in individual bunkers. Each constituent is withdrawn at a controlled rate and all are mixed in a blender before being taken to raw meal feed storage or direct to the kiln. Raw meal is sometimes granulated before it enters the kiln. This is said to reduce the dust generated in the kiln. It may also assist in controlling the raw meal rate through the kiln.

Calcination

Anhydrite kilns, like limestone kilns, can be fired with coal, oil or possibly gas. An anhydrite kiln is lined in the hotter zones with resistant bricks similar to those used in limestone kilns and, as with these kilns, fuel combustion air is preheated by cooling the clinker as it leaves the kiln. The SO_2-containing gas passes through the kiln smoke box and a cyclone to remove most of the entrained dust. The remainder of the dust can be removed in a Peabody Scrubber or in an electrostatic precipitator followed by towers as described in section C of chapter 2. The amount of recovered dust that can be recycled to the raw meal feed depends on its alkali content. This in turn depends on the amount of alkalis in the constituents of the raw meal. The higher the quantity of alkalis in the raw meal, the greater the proportion of dust that will have to be discarded.

As already explained, an anhydrite kiln, unlike a limestone kiln, does not run with an excess of oxygen in the kiln atmosphere. On the contrary, the oxygen content of an anhydrite kiln atmosphere is controlled carefully to promote the desired reactions in the kiln. The composition of the kiln exit gas is approximately: $SO_2 = 9\%$, $O_2 = < 1\%$, $CO_2 = 20\%$ and $N_2 = 70\%$.

A heat balance in an anhydrite kiln has not been calculated in the same detail as that for the limestone kiln. The heat required to produce 1 mole CaO from $CaSO_4$ by reduction with C is about 70 per cent more than that needed to produce 1 mole CaO from $CaCO_3$ by thermal decomposition. An anhydrite kiln therefore has a larger basic fuel requirement than a limestone kiln. In addition, heat recovery by suspension preheater or by Lepol kiln is not practised.

Ceramic dams and lifters are fitted in the kilns to control the rate at which meal passes through the kiln and improve contact between the burden and the hot gas in the kiln. This reduces the heat lost on the kiln exit gas but to a less extent than equipment used with modern limestone kilns. The thermal efficiency of an anhydrite kiln is therefore lower than that of a limestone kiln. This, coupled with the higher basic fuel requirement, gives a fuel requirement of about 1,800 t cal per ton of clinker, approximately twice that of a modern limestone kiln. A reduction in fuel requirement in an anhydrite kiln is beneficial not only in decreasing the cost of burning but also by increasing the SO_2 concentration in the kiln exit gas by reducing the $N_2 + CO_2$ resulting from the fuel combustion. This has advantages mentioned in section C of this chapter.

Current anhydrite kiln design indicates that an output of 100,000 tons of clinker per year should be achieved in a kiln 350 ft long by 12 ft in diameter. The minimum economic size for a developed country is now regarded as about 180,000 tons of clinker per year, for which a kiln 450 ft by 15 ft would be needed. It is most unlikely that a developing country would need more than 100,000 tons of H_2SO_4 per year at one time, or that it would be willing to install a kiln so much larger than the largest anhydrite kiln now operating in a developed country, which is about the size specified for 100,000 tons of clinker per year. It will be noted that the output of these anhydrite kilns is much less than that of a modern cement kiln using limestone and fitted with efficient heat recovery equipment.

Conversion of clinker to cement

Anhydrite clinker is converted to cement in the same way as limestone clinker (see section F of chapter 1).

Rapid hardening Portland cement

This can be made by fine grinding exactly as with clinker produced from limestone.

C. PRODUCTION OF SULPHURIC ACID FROM CALCIUM SULPHATE

Little need be said about the production of H_2SO_4 from the SO_2-containing gas leaving the kiln because this is essentially similar to production from pyrites described in section C of chapter 2. The wet gas cleaning system is controlled so that it removes any HF or HCl which may be present in the kiln gas, thus obviating the possibility of halogen poisoning of the vanadium oxidation catalyst. The wet substantially dust-free gas from the dust removal plant is passed through electrostatic precipitators to remove mist and the small amount of residual dust. Thereafter the gas is treated as described for gas made from pyrites, with air added before the drying tower to give the required O_2/SO_2 ratio. Some operators work with an O_2/SO_2 ratio of 1.6, which is higher than that used with gas made from pyrites. This high ratio reduces the SO_2 content of the gas entering the converter to little more than 5 per cent with corresponding increase in the size of gas drying towers, converter and heat exchangers. It should be possible to achieve a conversion of 98 per cent in a four-pass converter with a somewhat lower O_2/SO_2 ratio, but reduction of this ratio to little more than 1 may require some form of gas scrubbing to remove unconverted SO_2 from the stack gas. A decision between these alternatives must depend on a contractor's advice after full investigation of local circumstances and requirements.

The tail gas from the absorbers, whether scrubbed or not, is more misty than the tail gases from plants using sulphur or pyrites. This extra mistiness is connected with the synthesis of oxides of nitrogen in the anhydrite kiln which cannot be avoided. In developed countries, the only satisfactory method of producing an acceptable stack discharge is to pass the tail gas through electrostatic precipitators. The need for such precipitators in a developing country will depend on the location of the plant and local regulations. If tail gas precipitators are not installed when a plant is built, the layout should be planned to permit them to be added easily if this is found necessary.

D. CAPITAL COSTS

Capital cost estimates for anhydrite kilns are given in recent papers and publications: *European Chemical News* (1968), *Sulphur* (1968) No. 74 and M. W. Kellogg Company (1968). Estimated costs for different outputs have also been supplied by an engineering contractor. There are considerable differences between these various estimates. These may be partly due to differences in what the estimates include, for example, the amount provided for storage of raw materials and finished products, the inclusion or omission of a plant for cement manufacture, storage and packing and so forth. There may also be different opinions about the maximum size of single stream units and the cost reduction which these would make possible.

The capital costs given below are battery limit costs based on a kiln output of 100,000 tons of H_2SO_4 per year. They cover for moderate sulphuric acid storage and raw materials stored in the plant. They do not include raw material stores external to the plant or equipment for winning anhydrite but they do provide a plant for the grinding, storage and despatch of cement. Their accuracy is unlikely to be better than ± 25 per cent. Offsite costs as discussed in section D of chapter 2 add substantially to the battery limit costs.

Fixed capital costs

Output of H_2SO_4 (tons/year)	*Battery limit cost*	
	million £	*£/ton/year*
100,000	3.9	39
200,000	6.6	33
300,000	9.0	30

These costs should be increased by 10 to 12 per cent if mineral gypsum is used instead of anhydrite. The cost of transport and an allowance (if required) for higher civil and erection costs must be added (see section D of chapter 2).

Working capital

It is suggested that the working capital in a developing country should be taken as 10 per cent of the battery limit cost.

E. RAW MATERIAL AND OTHER REQUIREMENTS

Raw material and other requirements are expressed below in terms of the amount needed to produce one ton of H_2SO_4. This is also true for clinker production, thus, the figures given below are those for the production of one ton of H_2SO_4 and one ton of clinker. The requirements are expressed per ton of H_2SO_4 because it is usual in the cost evaluation to subtract the credit for clinker or cement from the total cost to give the cost of acid made.

Raw materials

The amount of anhydrite required depends on its purity and the alkali content of the raw meal, which determines how much dust can be recycled. If the anhydrite contains 90 per cent $CaSO_4$ and if 90 per cent of the sulphur in it is converted to H_2SO_4, the amount of anhydrite required is about 1.7 tons per ton of H_2SO_4. The ratio clinker/H_2SO_4 will vary slightly with the composition of the raw materials used but it is sufficiently accurate for preliminary evaluation to assume that 1 ton of clinker is made for each ton of H_2SO_4 produced.

The amounts of sand, shale, ashes and the like required for producing one ton of H_2SO_4 also depend on their composition. They are (expressed on dry basis) approximately as follows:

	Tons/ton of H_2SO_4
Anhydrite	1.70
Shale	0.35
or Sand	0.15
and Ash	0.15
Coke	0.10—0.14
Gypsum	0.03

Fuel

t cal/ton of H_2SO_4: 1,800

This will be increased by about 30 per cent if mineral gypsum is used.

Electricity

kWh/ton of H_2SO_4: 250—260

This includes cement grinding and packing and relates to plant producing 100,000 tons of clinker per year and 100,000 tons of H_2SO_4 per year. The power requirement will fall somewhat with increase in output if this is achieved by installing larger kilns.

Water

m^3/ton of H_2SO_4: 70—85

Steam

tonnes/ton of H_2SO_4: 0.15—0.20

Compressed air

m^3/ton of H_2SO_4: 100—350

Maintenance

The maintenance cost is taken as 5 per cent of the battery limit cost. This is £1.95 per ton of H_2SO_4 for an output of 100,000 tons of H_2SO_4 per year. It will diminish with increasing output.

Process labour and supervision

The numbers of process operators and supervisors in existing anhydrite kiln plants do not appear to have been published. One estimate of process labour and supervision in a plant to produce 300,000 tons of H_2SO_4 per year is 0.92 man-hours per ton of H_2SO_4 (Ashburner, 1968). A plant producing 100,000 tons of H_2SO_4 per year would not show a pro rata reduction in total man-hours. On the assumption that process labour and supervision requirements would be halved for one third of the output (i. e. 100,000 tons of H_2SO_4 per year), these would amount to 1.5 man-hours per ton of H_2SO_4. This does not include mining or quarrying the raw materials or grinding and packing cement. About 0.3 man-hours must be added if cement is ground and packed, giving a total requirement of 1.8 man-hours per ton of H_2SO_4 for the plant from raw material reception to cement packing.

In comparing these man-hour requirements in a developed country with those for a limestone kiln in a developing country (cf. section H of chapter 1), it must be remembered that the latter figures include personnel for administration, security and miscellaneous, which are not included in the man-hour requirements for an anhydrite kiln. A complete breakdown of the labour force for the limestone kiln in a developing country is given in *Studies in Economics of Industry* (United Nations, 1963, p. 21).

The process labour and supervision requirements in a developing country will depend on the skill of the workers available and the extent to which the plant is instrumented and mechanized. It must be appreciated that the control of an anhydrite kiln is a difficult operation calling for a high degree of technological competence. A developing country would find it necessary to train supervisors and kiln burners on an existing kiln plant. A burner from a limestone kiln would require some training on an anhydrite kiln before he could be given charge of an anhydrite kiln. A developing country would also require the help of a considerable number of expatriate operators skilled in the art of running an anhydrite kiln to start up the plant, and to train the rest of the plant personnel. The cost of commissioning and proving the plant, the training of operatives and the provision of skilled expatriate labour cannot be estimated at this stage, but it will be considerable.

Depreciation

This has been taken as 10 per cent of the battery limit cost and amounts to £3.9 per ton of H_2SO_4 at an output of 100,000 tons per year.

Packaging and transport

The statements made in section I of chapter 1 apply equally to cement made from anhydrite.

Overhead costs

A figure must be included to cover this item. A provisional and approximate method for preliminary evaluation has been suggested in section I of chapter 1.

Interest payments—return on equity capital

These have been discussed in section I of chapter 1. The appropriate figures are included here.

Summary

Requirements for production of 1 ton of H_2SO_4:

Anhydrite (tons)	1.70
Shale (tons)	0.35
or sand (tons)	0.15
and ash (tons)	0.15
Coke (tons)	0.10—0.14
Gypsum (tons)	0.03
Fuel (t cal)	1,800
Electricity (kWh)	250—260
Water (m^3)	70—85
Steam (tonnes)	0.15—0.20
Compressed air (m^3)	100—350
Maintenance (£)	1.95
Process labour and supervision, (man-hours)	1.50
Depreciation (£)	3.90
Clinker, 1 ton	Credit based on realization

Overhead charges, about 100 per cent of labour costs
Packaging and transport
Interest payments and loan repayment } to be added
Return on equity capital
The cost of commissioning and personnel training must also be included (cf. section I of chapter 1).

A preliminary estimate of the production cost can be made from these figures, but it must be emphasized again that a detailed evaluation of a project by a contractor must be made to obtain an accurate cost estimate. This must be combined with forecast production and sales estimates of cement and sulphuric acid to obtain an over-all assessment of the viability of the project. It may take at least a year to achieve steady operation at design output in a developing country.

Conclusions

The capital invested in an anhydrite kiln plant is very high and the capital charges are correspondingly heavy. The plant must operate at, or near to capacity if economic production is to be achieved. For example, operation at half the design output would double the already heavy capital charges. It must also be remembered that the output of clinker from an anhydrite kiln is low by comparison with modern kilns working on limestone and that an anhydrite kiln is therefore a more expensive producer of clinker.

Pure anhydrite contains only 23.5 per cent sulphur and an anhydrite kiln must therefore be situated at, or near to the quarry or mine producing it to avoid heavy transport charges which could make a project uneconomic. Since 1.7 tons anhydrite are used for each ton of H_2SO_4 made, the cost of anhydrite at the kiln plant is of major importance to the economic viability of a project. If anhydrite is not already produced, it could be won most cheaply by quarrying. Drift mining would be more costly than quarrying but cheaper than a shaft mine, which could add very considerably to the over-all cost of the project. The method adopted would, of course, depend on the nature of the deposit.

It must also be appreciated that cement and sulphuric acid are both relatively low cost products which cannot bear heavy transport charges. A market for them must therefore exist within a relatively short distance of the anhydrite kiln plant. Since one ton of clinker is made for each ton of H_2SO_4 produced, the price obtained for the clinker or cement made from it will have a marked effect on the economics of an anhydrite kiln plant.

It may be of interest to note that a recent production cost estimate for a plant to make 330,000 tonnes of H_2SO_4 per year from anhydrite in a developed country indicated that sulphuric acid from this plant would be competitive with sulphuric acid from a sulphur plant when the price of elemental sulphur exceeded $45 per ton (McFarlane, 1968, p. 34).

APPENDIX 1

Operators of anhydrite-sulphuric acid plants and their engineering contractors

The operators of anhydrite-sulphuric acid plants are listed below, so far as they are known, with the number of kilns at each location and their total capacity. The engineering contractors appointed by the operators are also indicated. A serious inquirer for the anhydrite-sulphuric acid process whose preliminary evaluation based on the data in this report indicates that the process might be economically attractive can obtain further assistance from an engineering contractor.

Albright and Wilson Limited,
Marchon Division,
Whitehaven,
Cumberland,
United Kingdom

Number of kilns — 5
H_2SO_4 capacity — 400,000 t/yr
Clinker capacity — 380,000 t/yr

Engineering contractor

Power-Gas Corporation Limited,
P.O. Box 21,
Bowesfield Lane,
Stockton-on-Tees, Teesside,
United Kingdom

Imperial Chemical Industries Limited,
Agricultural Division,
Billingham, Teesside,
United Kingdom

Number of kilns — 3
H_2SO_4 capacity — 190,000 t/yr
Clinker capacity — 187,000 t/yr

Engineering contractor

Simon-Carves Chemical Eng.
Limited,
P.O. Box 49,
Stockport, Cheshire,
United Kingdom

Österreichische Stickstoffwerke, AG,
Postfach 296,
A-4021 Linz,
Austria

Number of kilns — 1
H_2SO_4 capacity — 68,000 t/yr
Clinker capacity — 66,000 t/yr

Engineering contractors

E.I.C. Engineering and Industrial Corporation S.A.,
31 Boulevard Prince Henri,
Luxembourg

Fredrich Krupp,
Chemieanlagenbau,
Postfach 979,
D-43 Essen,
Federal Republic of Germany

The M. W. Kellogg Company,
711 Third Avenue,
New York, N.Y. 10017,
United States of America

Vereinigte Österreichische Eisen- und Stahlwerke AG,
Postfach 2,
A-4021 Linz,
Austria

United Sulphuric Acid Corporation Limited,
Widnes, Lancashire,
England

Number of kilns — 2
H_2SO_4 capacity — 200,000 t/yr
Clinker capacity — 190,000 t/yr

Engineering contractor

Simon-Carves Chemical Eng. Limited,
P.O. Box 49,
Stockport, Cheshire,
United Kingdom

V. E. B. Chemiewerk,
Coswig,
German Democratic Republic

Number of kilns — 4
H_2SO_4 capacity — 240,000 t/yr
Clinker capacity — 230,000 t/yr

V. E. B. Farben Fabrik,
Wolfen,
German Democratic Republic

Number of kilns — 4
H_2SO_4 capacity — 220,000 t/yr
Clinker capacity — 210,000 t/yr

Engineering contractors

V. E. B. Chemie-Ingenieurbau,
Leipzig,
German Democratic Republic

Simon-Carves Chemical Engineering Limited,
P.O. Box 49,
Stockport, Cheshire,
United Kingdom

Zakłady Chemiczne,	Number of kilns — 2
Wizów,	H_2SO_4 capacity — 114,000 t/yr
Poland	Clinker capacity — 116,000 t/yr

Design work for Zakłady Chemiczne Wizów is carried out by "Biprokwas", i.e. Biuro Projektów Przemysłu Nieorganicznego, M. Strzody 11, Gliwice, Poland. The services of "Biprokwas" can be obtained by companies outside Poland through "Polimex", i.e. Polskie Towarzystwo Exportu i Importu Maszyn, Sp. z o.o., Czackiego 7—9, Warsaw, Poland.

APPENDIX 2

THERMOCHEMICAL DATA

(1) $CaSO_4 = CaO + SO_2 + \frac{1}{2} O_2.$
$\Delta H^0_{298} = +119.6$ kcal/mole

(2) $CaSO_4 + 2C = CaS + 2CO_2.$
$\Delta H^0_{298} = +39.0$ kcal/mole

(3) $3CaSO_4 + CaS = 4CaO + 4SO_2$
$\Delta H^0_{298} = +251.2$ kcal/mole

(4) $CaS + 2SO_2 = CaSO_4 + S_2$
$\Delta H^0_{298} = -54.6$ kcal/mole

4. PORTLAND CEMENT FROM BY-PRODUCT CALCIUM SULPHATE

A. PRODUCTION OF BY-PRODUCT CALCIUM SULPHATE

A developing country may wish to produce a substantial amount of sulphuric acid largely or wholly for fertilizer manufacture and lack indigenous supplies of mineral calcium sulphate. If plans for fertilizer production include the manufacture of phosphatic fertilizers, the developing country can set up a fertilizer complex that would be largely self-sufficient in sulphuric acid.

The manufacture of phosphoric acid from phosphate rocks by reaction with sulphuric acid and the conversion of the phosphoric acid into ammonium phosphates are well known processes. The ammonium phosphates can be mixed with ammonium nitrate and potassium salts to give "complete" fertilizers containing the three major plant foods, nitrogen, phosphorus and potassium. Phosphate rocks are essentially impure apatites chiefly fluorapatites [$3Ca_3(PO_4)_2 \cdot CaF_2$], which react with sulphuric acid to give phosphoric acid and calcium sulphate, which may be in the forms of gypsum, hemihydrate or anhydrite. Most of the existing phosphoric acid plants produce calcium sulphate as gypsum but an increasing number of new plants make hemihydrate. Calcium sulphate in whatever form it is made is removed from the phosphoric acid by filtration and put to dump or occasionally used for the manufacture of plaster and plasterboard. The amounts of phosphate rock and sulphuric acid used and of phosphoric acid and calcium sulphate produced will depend on the phosphate rock used, but the round figures given below show the order of usages and production.

	tons/year
Phosphate rock	120,000
Sulphuric acid	100,000
Phosphoric acid (as P_2O_5)	40,000
Calcium sulphate (as "dry" gypsum) .	180,000

The calcium sulphate contains a minimum of about 20 per cent of free water when it leaves the filters.

Theoretically, the by-product calcium sulphate can be used in a kiln process to regenerate the sulphuric acid used to make the phosphoric acid, but in practice, it would be necessary to burn a small amount of sulphur or anhydrite in the kiln to compensate for the inefficiencies which inevitably occur. The by-product calcium sulphate will contain impurities from the phosphate rock which could affect the quality of cement made from it. The most important of these are phosphate and fluorine. P_2O_5 is present in by-product calcium sulphate partly in a water-soluble form and partly as a solid solution in gypsum which is water-insoluble. The fluorine may be present as CaF_2 or in more complex forms such as fluosilicates. The P_2O_5 and F contents of by-product gypsum vary with the phosphate rock and process used, but can be between 0.5—2.0 per cent of P_2O_5 and 0.1 — 1.5 per cent of F (dry basis).

The effect of P_2O_5 and F on Portland cement quality must be considered before the use of by-product calcium sulphate for the manufacture of cement and sulphuric acid can be discussed.

B. THE EFFECT OF PHOSPHORUS PENTOXIDE AND FLUORINE ON THE QUALITY OF CEMENT MADE FROM LIMESTONE

Phosphorus pentoxide

It has long been known in the manufacture of Portland cement from limestone that P_2O_5 in significant amounts in the raw materials, that is, producing 1 — 2 per cent of P_2O_5 in the cement, gives a raw meal that is hard to burn to a low free lime content and reduces the rate at which early-strength develops in the resulting cement; the setting time of this cement is erratic. Precise information was lacking until the findings of Nurse (1952). Nurse's research and that by other workers in this field were reviewed by Steinour (1957). Steinour believed that Nurse's equations and conclusions regarding the phase composition of phosphate containing clinker could be accepted as approximately valid and that the results of other workers, properly interpreted, did not conflict with Nurse's conclusions. Nurse's research can therefore be regarded as representative of results up to 1957, when Steinour's review was published.

The existence of compounds such as silicocarnotite ($5\,CaO \cdot P_2O_5 \cdot SiO_2$) and nagelschmidtite ($7\,CaO \cdot P_2O_5 \cdot 2SiO_2$) has long been known. These can be written using the normal abbreviations and with P representing P_2O_5, as $C_3P \cdot C_2S$ and $C_3P \cdot 2C_2S$ respectively. In fact, both these phases have been shown to be solid solutions between C_3P and C_2S and can thus vary considerably in composition. Since C_2S is an important constituent of Portland cement, this suggested that P_2O_5 in a phosphate-containing cement might be present as a solid solution of C_3P with C_2S.

Nurse, investigating the proposed manufacture of cement in Uganda from phosphatic limestone, examined the effect of P_2O_5 on the burning of Portland cement clinker and the setting and hardening of the resulting cement. He found that P_2O_5 in the limestone, or C_3P added to synthetic mixes, formed a solid solution with C_2S in the cement clinker. Nurse established that the composition of the solid solution (P_{SS}) which exists in equilibrium with C_3S and CaO at 1,400° C was approximately: $P_2O_5 = 7$ per cent; $SiO_2 = 26.5$ per cent; $CaO = 66.5$ per cent (equivalent to 1 $C_3P : 8.95\ C_2S : 3.15\ C$).

Steinour summarized Nurse's findings in the table below. The equilibria are those which would be obtained with slow cooling to the point of complete crystallization. The "lime saturation" of this table is therefore not the "lime saturation factor" defined in the cement specification (see section D in chapter 1).

Clinker constitution when phosphate is present

Below lime saturation	*At lime saturation*	*When lime is in excess*
C_4AF	C_4AF	C_4AF
C_3A	C_3A	C_3A
$\left.\begin{matrix}P_{SS}\\C_2S\end{matrix}\right\}$ ss	P_{SS}	P_{SS}
	—	—
C_3S	C_3S	C_3S
—	—	C

C_2S exists below lime saturation as a solid solution with P_{SS}. The amount of C_2S decreases as lime saturation is approached and becomes zero at lime saturation. Further increase in lime gives free CaO. If P_{SS} were not shown in the table, the three columns would represent the components produced from normal raw meal. The presence of P_2O_5 means that P_{SS} will also form and will withhold fixed amounts of CaO and SiO_2 from other reaction. The remaining CaO and SiO_2 will react in the normal way to form C_2S and C_3S, except that C_2S goes into solid solution with P_{SS}.

The ratio of CaO/SiO_2 in P_{SS} is less then in C_3S and lime saturation therefore occurs at a lower lime content when P_2O_5 is present. In fact, each per cent of P_2O_5 reduces the CaO limit by 1.1 per cent. Thus a producer operating at what would be a feasible lime content for a normal raw meal will find himself operating closer to or even above the lime limit if P_2O_5 is present, although his product contains less C_3S. This explains the difficulty experienced in burning raw meal containing P_2O_5 to a low free lime content.

Nurse derived equations for calculating the compound composition of cements containing C_3P, assuming equilibrium conditions had been attained at 1,400° C and complete crystallization had ensued thereafter. As previously stated in the appendix to chapter 1, the compound content of normal cement is given by these equations, where the formula in parentheses represents the weight percentage of that compound in the cement.

$$
\begin{aligned}
C_4AF &= 3.04\,(Fe_2O_3)\\
C_3A &= 2.65\,(Al_2O_3) - 1.69\,(Fe_2O_3)\\
C_3S &= 4.07\,(CaO) - 7.60\,(SiO_2) - 6.72\,(Al_2O_3) - 1.43\,(Fe_2O_3)\\
C_2S &= 8.60\,(SiO_2) - 3.07\,(CaO) + 5.10\,(Al_2O_3) + 1.08\,(Fe_2O_3)
\end{aligned}
$$

Nurse recalculated these equations to allow for P_2O_5 to give those shown below in which (P_2O_5) = per cent of P_2O_5 in cement. These equations are identical with the normal equations except for the P_2O_5 factor.

$$C_4AF = 3.04\ (Fe_2O_3)$$
$$C_3A = 2.65\ (Al_2O_3) - 1.69\ (Fe_2O_3)$$
$$C_3S = 4.07\ (CaO) - 7.60\ (SiO_2) - 6.72\ (Al_2O_3) - 1.43\ (Fe_2O_3) - 9.9\ (P_2O_5)$$
$$C_2S = 8.60\ (SiO_2) - 3.07\ (CaO) + 5.10\ (Al_2O_3) + 1.08\ (Fe_2O_3 - 3.4\ (P_2O_5)$$
$$P_{SS} = 14.3\ (P_2O_5)$$

The reason for the marked effect of P_2O_5 on the rate at which cement hardens is apparent from the equation for determining C_3S content (see section C in chapter 1) that is largely responsible for the early strength of cement. Each per cent of P_2O_5 reduces the C_3S content by 9.9 per cent. Nurse confirmed the accuracy of his calculations by measuring the percentages of each constituent in synthetic clinkers.

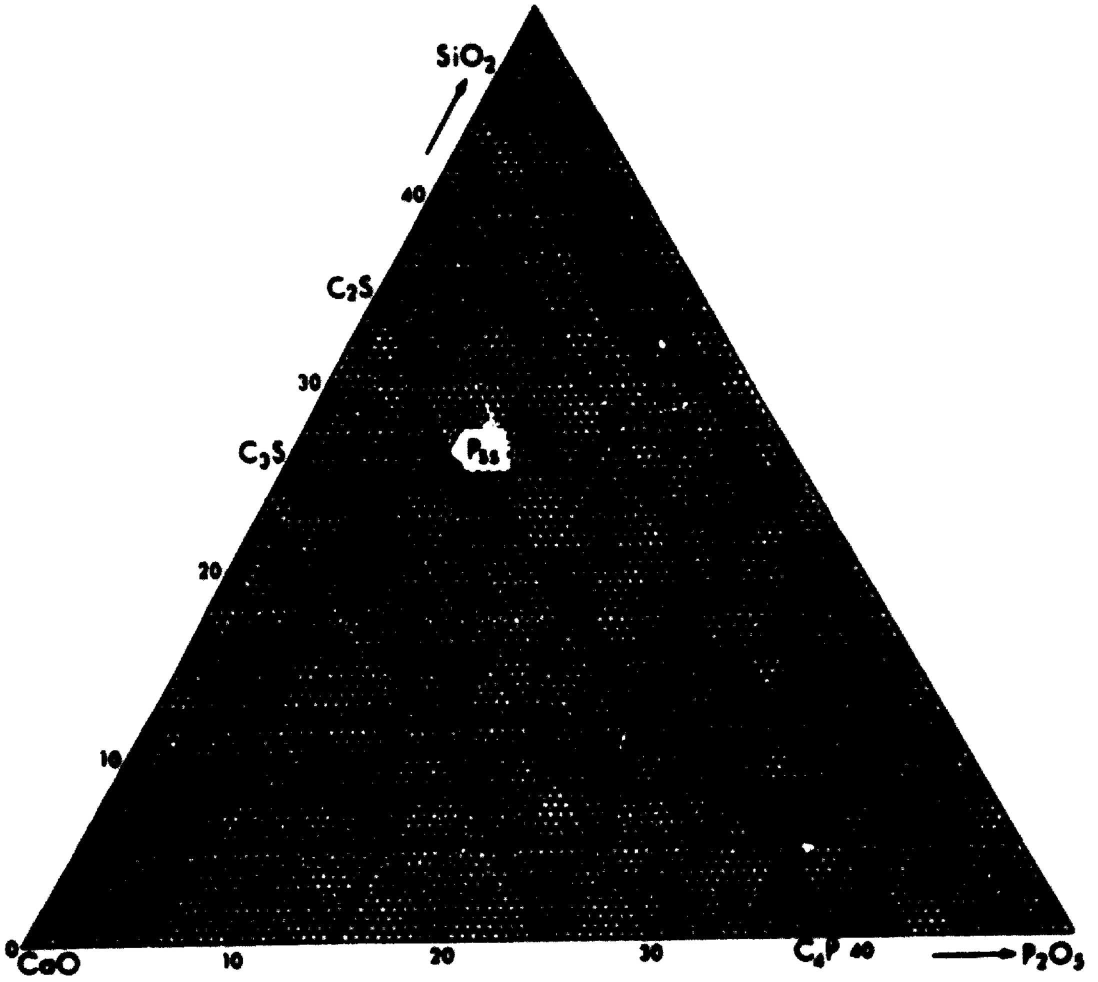

Figure 15. Approximate solid phase relations in system CaO—P_2O_5—SiO_2 in contact with C_3A and C_4AF at 1,400°C

Steinour somewhat extended a diagrammatic representation of the clinker equilibria made by Nurse and this is shown in figure 15. In using this diagram, the CaO required to form C_4AF and C_3A is first calculated and subtracted from the total CaO. The residual CaO, together with the SiO_2 and P_2O_5, are then recalculated to give a total of 100 per cent. The phases to be expected in solidified clinker of this composition (in addition to C_4AF and C_3A) can then be determined from figure 15. The point P_{SS} represents the limiting composition of the solid solution (P_2O_5 = 7 per cent, SiO_2 = 26.5 per cent, CaO = 66.5 per cent) and the line joining P_{SS} and C_2S represents the solid solutions formed by these two end members. Any point within the triangle C_3S—P_2S—P_{SS} can be resolved into definite percentages of C_3S, C_2S and P_{SS}, the two latter being united in the over-all solid solution phase. Properly designed mixes will thus be represented by points in the triangle C_3S—C_2S—P_{SS}. Over-limed mixes will normally fall in the triangle C_3S—CaO—P_{SS} but over-limed mixes containing as much as 6 or 7 per cent P_2O_5 might fall in the triangle CaO—P_{SS}—C_4P, in which case C_3S would not be present (C_4P = tetracalcium phosphate, $4\,CaO \cdot P_2O_5$).

Since P_2O_5 reduces the amount of C_3S that can be present in the clinker, Nurse concluded that mixes should be made up to give approximate lime saturation in the clinker, thus achieving the maximum possible C_3S content. This would place them on the line C_3S—P_{SS} in figure 15. To help in computing mixes, Nurse developed an equation that would produce lime saturation when using a raw mix of limestone (*L*) and clay (*C*). In the equation below, the percentages of the oxides in these raw materials are indicated by their formulae in parentheses, with the respective suffixes *L* or *C*; Δ is used to indicate differences, the percentage in clay being always subtracted from that in limestone. Thus, $(\Delta\,SiO_2) = (SiO_2)L - (SiO_2)C$. $(\Delta\,SiO_2)$ would of course usually be negative.

The percent clay in a mix to give saturation is given by:

$$\%\ \text{clay} = \frac{100\,(CaO)_L + 100\,(P_2O_5)_L - 277\,(SiO_2)_L - 165\,(Al_2O_3)_L - 36\,(Fe_2O_3)_L}{(\Delta CaO) + (\Delta\,P_2O_5) - 2.77\,(\Delta\,SiO_2) - 1.65\,(\Delta\,Al_2O_3) - 0.36\,(\Delta\,Fe_2O_3)} \qquad (7)$$

This equation of Nurse apparently makes possible a rational design of mix that will produce a phosphate-containing clinker without excessive free lime and with a satisfactory C_3S content.

Nurse examined the physical properties of P_2O_5-containing cements and showed that cement made in the laboratory from natural raw materials to give a lime saturation factor of 1 failed to meet the BS 12 : 1947 compressive strength specification if the P_2O_5 content exceeded 2.25 per cent.[7] The initial and final

---

[7] BS 12 : 1947 required the compressive strengths of vibrated mortar cubes to be 1,600 lb/in² (3 days) and 2,500 lb/in² (7 days). These figures were increased to 2,200 lb/in² (3 days) and 3,400 lb/in² (7 days) in BS 12 : 1958 (see section D in chapter 1). These higher compressive strengths would have reduced the P_2O_5 content of cement to about 1.75 per cent. As pointed out in chapter 1, a cement that just met BS 12 : 1958 strength specifications would be at a competitive disadvantage in the United Kingdom.

setting times increased considerably with P_2O_5 content but met BS 12: 1947 (and BS 12: 1958). Nurse also showed that the strength of concrete made from P_2O_5-containing cement fell off more rapidly with increasing water/cement ratio than that made from ordinary cement.

Welch and Gutt (1962) reported that manufacturing experience in Uganda had shown that the effect of P_2O_5 was less deleterious than had been forecast from Nurse's laboratory and pilot plant work. A possible reason for this is discussed below but, whatever the cause, the reduction in the expected deleterious effect of P_2O_5 in the full scale plant, combined with the addition of fluorspar to the kiln feed, enabled cement of excellent quality to be made.

It is now necessary to discuss why the effect of P_2O_5 in the full scale plant was less harmful than Nurse expected. Nurse (1952) and Nurse, Welch and Gutt (1959) showed that β-, α'-, and α-forms of C_2S could be stabilized by P_2O_5. Welch and Gutt (1962) also showed that only P_2O_5-stabilized β-form of C_2S had substantial hydraulic properties. In fact, P_2O_5 enhanced the hydraulicity of β-form of C_2S. These workers considered that the reduction in deleterious effect of P_2O_5 in full scale manufacture in Uganda might be due to stabilization of β-form of C_2S by P_2O_5. They found that small amounts of P_2O_5 increased the compressive strength of synthetic C_2S while large amounts reduced it. This is apparently due to the fact that C_2S, in the absence of P_2O_5, was in the γ-form, with 2 per cent of P_2O_5 it was in the β-form and with 7 per cent and 15 per cent of P_2O_5 it was in the α'- and α-form respectively. They suggested that the detrimental effect of P_2O_5 on cement quality might be due to the presence of P_2O_5-stabilized α'-form of C_2S as well as to reduction in C_3S content to which it was attributed by Nurse. The beneficial action of fluorspar may result from the immobilization of some P_2O_5, the residual "free" or "active" P_2O_5 being below the level required for α'-form of C_2S stabilization, but above that required for β-form of C_2S stabilization.

Welch and Gutt also examined the effect of P_2O_5 on C_3S. They found that the compressive strength of synthetic C_3S diminished with addition of up to 1 per cent of P_2O_5 (as C_3P). increased with between 1 — 2 per cent of P_2O_5 to slightly more than with nil P_2O_5 (except for one-day strength) and then decreased as the P_2O_5 was raised above 2 per cent. This decrease may be due to an increasing proportion of α'-form of C_2S produced at the higher P_2O_5 contents. C_3S would then be diluted with non-hydraulic α'-form of C_2S. Welch and Gutt calculated that the α'-form of C_2S content with 2 per cent of P_2O_5 addition was about 30 per cent. Since the hydraulicity of this mixture is comparable with that of pure C_3S, they suggest that the form of C_3S present in this mix has an enhanced hydraulic value. The addition of 2 per cent of P_2O_5 to synthetic C_3S reduced the lower temperature at which C_3S decomposition occurred from 1,250° C to 1,160° C.

Welch and Gutt state that subjective estimates of cement quality based on microscopic examination of the phases present in the clinker cannot be wholly reliable. This is because minor components of cement such as P_2O_5 (and fluorine, see below) are capable of causing profound structural modification of C_2S and

C_3S. Since atomic arrangement plays an extremely important part in determining the way in which water enters the crystal lattice and develops hydraulicity, the role of minor components in modifying crystal lattices plays a much more important part in cement quality than the amount in the clinker might suggest. It is therefore necessary to establish the precise properties of these modified phases and, in particular, their latent hydraulicity.

The effect of water-soluble P_2O_5 on cement quality must be briefly considered. Alkali metal phosphates very greatly retard the setting and hardening rate of cement. Nurse extracted only traces of P_2O_5 from his P_2O_5-containing cements by shaking them with ten times their weight of water. Steinour thought that this did not exclude the possibility of a water-soluble phosphate dissolving and precipitating a new compound as rapidly as it dissolves. He agreed that if all the P_2O_5 is present as a solid solution of P_{SS} with C_2S, there was no reason to expect more than traces of P_2O_5 to dissolve in water, but he considered that it would be unwise to dismiss as of no possible pertinence the marked effects produced by water-soluble P_2O_5. There is no guarantee that under any and all circumstances, all the P_2O_5 in clinker will be in the solid solution.

It is clear from the Uganda experience that good quality Portland cement can be made from phosphatic limestone, especially if fluorspar is added. It is also clear that the effects of P_2O_5 are more complicated than Nurse thought and the last paragraph of Steinour's review (1957) is relevant: "Adequate experimentation with the particular raw materials that would be used should obviously precede commercial production of cement having a significant content of phosphate. It does appear, however, that the way has been opened for more intelligent testing of this kind with much promise of a successful outcome if the P_2O_5 content of the clinker can be kept below 2 or 2.5 per cent."

Fluorine

Fluorspar, CaF_2, has occasionally been used as a kiln flux (in P_2O_5-free cement raw meal) because it lowers the temperature at which liquid appears, thus reducing the clinkering temperature.

An addition of 5 per cent CaF_2 to cement raw meal reduced the temperature of liquid formation by several hundred ° C and the clinkering temperature by 120° to 150° C but CaF_2 greatly accelerated the rate of decomposition of C_3S below 1,250° C. Clinker made in the presence of CaF_2 must therefore be cooled rapidly to prevent C_3S decomposition. In addition, it increased the proportion of γ-form C_2S at the expense of β-form C_2S. For these reasons, it is rarely used as flux.

Later work by Welch and Gutt (1962) showed that the addition of fluorine (as CaF_2) to C_2S did not stabilize α'- or α-form of C_2S but that both these compounds were detected in synthetic C_3S to which fluorine had been added, when the fluorine content exceeded 0.74 per cent. They also found that fluorine greatly accelerated the rate at which synthetic C_3S was produced at 1,550° C. Some fluorine was lost on heating to 1,550° C.

The compressive strength of synthetic C_3S (except for some unexplained anomalies in the 28-day strength) decreased with increasing fluorine content up to 1.74 per cent F. The presence of α'- and α-form of C_2S must contribute to this over-all fall in strength but Welch and Gutt believe that the major effect on strength results from structural changes introduced into C_3S by fluorine which reduce hydraulicity.

Earlier laboratory experiments on the addition of CaF_2 to phosphatic clinkers had shown that compressive strength did not rise proportionately to C_3S content. This lack of correlation between C_3S content and strength is partially explained by the above results which show that, although fluorine facilitates the formation of C_3S, the fluorinated phase becomes less hydraulic.

The net effect of fluorine addition to clinker is therefore beneficial only if the advantage of greater output outweighs the loss in quality, unless of course P_2O_5 is present in appreciable amounts in the raw meal. Even then care must be exercised because Welch and Gutt, in laboratory experiments on the addition of CaF_2 to raw meal containing 1.62 per cent of P_2O_5, showed that the compressive strength of the resulting cement (after addition of 1, 2, 3 und 4 per cent gypsum as retarder) fell to a minimum in the region of 0.8 — 1.27 per cent F in the cement and then rose again at higher fluorine levels. Welch and Gutt say that this behaviour suggests that optimum performance of the cement could be achieved, at least under laboratory conditions, by careful control of the phosphate and fluorine content, and equally that considerable falls in strength might occur through unsuitable proportioning of these components. The gypsum addition had a marked effect on strength development, the reduction in strength being markedly accentuated by increased gypsum addition. The reasons for this effect are unknown. The setting times were not determined. These results emphasize the importance of the minor components of cement in modifying the behaviour of a cement through their effect on the principal constituents. In particular, CaF_2 does not merely act as a flux but produces structural changes which have considerable influence on hydraulicity.

C. USE OF BY-PRODUCT CALCIUM SULPHATE FOR CEMENT AND SULPHURIC ACID PRODUCTION

Small-scale work

Simanovskaya and Shpent (1955, p. 917) examined in the laboratory the production of Portland cement clinker containing 3 per cent to 15 per cent of P_2O_5 from gypsum produced as a by-product of phosphoric acid manufacture with addition of tricalcium phosphate, and showed that P_2O_5 did not affect the dissociation of calcium sulphate (cf. Stinson and Mumma, 1954). They, like Nurse, found that lime saturation occurred at a lower lime content in the presence of P_2O_5 in mixes containing $CaCO_3$, $CaSO_4$ or by-product gypsum. The production of clinker of acceptable strength from by-product gypsum therefore required careful control of the lime content of the raw meal. Clinker containing 3 per cent of P_2O_5 made in the laboratory from by-product gypsum gave cement that had tensile strengths at 3, 7, 28 and 90 days similar to those of cement produced in the laboratory from $CaCO_3$ and to factory-made cement.

This laboratory work was followed by semi-plant experiments in a rotary kiln 7 metres long in which several tons of Portland cement were made from P_2O_5-containing raw meal. These semi-plant experiments confirmed that the presence of calcium phosphates in raw meal did not interfere with the dissociation of $CaSO_4$ nor prevent the production of high quality Portland cement but did require careful control of the lime content of raw meal.

Simanovskaya and Vodzinskaya (1955, 1956) examined in the laboratory the effect of fluorine, as fluorspar, on clinker produced from calcined by-product gypsum. The free lime content of clinker containing 3 per cent of P_2O_5 was reduced from 5.5 per cent to nil by the incorporation of 0.75 per cent of CaF_2 in the raw meal and the C_3S content (determined by microscopic examination[8]) rose from 20 per cent to 61 per cent. Clinker containing 5 per cent of P_2O_5 required the addition of 3 per cent of CaF_2 to raw meal to give cement that did not contain free lime. The C_3S content simultaneously increased from 6 per cent to 44 per cent. Similar results were obtained from raw meals based on $CaCO_3$ and $CaSO_4$ in which tricalcium phosphate was incorporated. Clinkers containing 10 per cent of P_2O_5 and 15 per cent of P_2O_5 made from by-product gypsum did not contain C_3S even when 3 per cent of CaF_2 was incorporated in the raw meal.

The authors conclude:

(1) As the P_2O_5 content of clinker increases from 0 to 15 per cent of P_2O_5 C_3S progressively disappears to give free CaO and C_2S which forms solid solutions with C_3P. These changes are already apparent to a considerable degree at 3 per cent of P_2O_5 in clinker and clinker containing 15 per cent of P_2O_5 contains scarcely any of the usual minerals of Portland cement clinker.

(2) It is possible to obtain Portland cement of standard quality from clinker containing 3 to 5 per cent of P_2O_5 which has been made from raw meal with a limited lime content. The ratio C_3S/C_2S in such clinker is 1.2 — 1.4 : 1.

(3) The addition of small amounts of fluorine as CaF_2 in the presence of P_2O_5 (3 — 5 per cent of P_2O_5 in the clinker) stabilizes C_3S and enables cement to be produced which contains 50 — 60 per cent of C_3S with no free lime.

The compressive strengths of cement made from clinker containing 3 per cent of P_2O_5 are similar to those of plant-produced cements. The Russian test for compressive strength is not identical with BS 12 : 1958 but it seems probable that cement made as described above and containing 3 per cent of P_2O_5 would satisfy BS 12 : 1958, although it might not meet the requirements of users to whom early high-strength is essential.

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[8] Cf. statement of Welch and Gutt (1962) on estimation of cement quality by microscopic examination of the phases present in clinker referred to earlier in section B of this chapter.

These conclusions are broadly in line with those given in section B of this chapter. The amount of P_2O_5 that can be tolerated in raw meal made from by-product gypsum is limited. The stabilizing action of CaF_2 on the C_3S in P_2O_5-containing clinker requires the incorporation of small amounts only of CaF_2 in raw meal. It would seem to follow from this that the absolute amount of CaF_2 in raw meal, and/or the P_2O_5/CaF_2 ratio in it, must be carefully controlled.

Large-scale work

As far as is known, by-product gypsum is not currently used as a source of calcium sulphate at any producing plant, but full-scale trials have been made. The results of these trials have not been published in detail because the information obtained from them is largely regarded as the confidential know-how of the companies concerned.

The main difference when the process is operated on by-product gypsum instead of anhydrite lies in the treatment of the by-product gypsum before it is incorporated into the raw meal. By-product gypsum is usually finely divided and therefore does not normally need grinding. It is partially or completely dehydrated, as with mineral gypsum, and taken to storage bunkers. By-product gypsum loses some fluorine during dehydration and wash towers are installed after the dust cyclones to prevent the discharge of fluorine to atmosphere. The other constituents of raw meal are dried, ground separately and taken to separate storage bunkers. The components of raw meal are withdrawn from these storage bunkers in the correct proportions (making allowance for the SiO_2, Al_2O_3 and Fe_2O_3 present in the gypsum) mixed and fed to the kiln through raw meal storage bunkers. Alternatively, the ingredients of raw meal other than by-product gypsum are mixed and subsequently blended with the dehydrated gypsum. The kiln firing temperature is slightly lower than with anhydrite, presumably due to the fluxing action of CaF_2 in the raw meal.

Zakłady Chemiczne Wizów, Poland, claim to have made the first tests on by-product gypsum in a kiln normally operating on anhydrite and producing 150 tons of H_2SO_4 per day and 150 tons per day clinker. A run of two days was made in 1964 and another of ten days in 1967. Two raw meals were used in these tests, one incorporating a fifty-fifty mixture of anhydrite and by-product gypsum and the other by-product gypsum only. The ratio of clinker to H_2SO_4 is about 0.9 with by-product gypsum. These full-scale tests established the best conditions for the control of the kiln, showed that fluorine entering the gas stream from the gypsum could be removed (thus preventing poisoning of the vanadium oxidation catalyst) and determined the permissible P_2O_5 content of by-product gypsum for production of clinker which met the Polish "350" specification. The compressive strength required by this specification seems slightly below that of BS 12:1958.

As a result of these tests, Polimex is in a position to supply know-how for a plant to make sulphuric acid and clinker from by-product gypsum, alone or mixed with anhydrite. The know-how includes specifications for the raw materials and finished products and for plant equipment. They will give technical assistance during the erection and commissioning of a plant and train a purchaser's personnel in the operation of a kiln on by-product gypsum. Polimex in its "Preliminary Offer for the Production of Sulphuric Acid and Cement Utilizing Phospho-Gypsum as the Raw Material" regards plant to produce 100,000 tons of H_2SO_4 per year as the minimum economic size.

V. E. B. Chemiewerk, Coswig, German Democratic Republic, have also done full-scale tests on the use of by-product gypsum in a kiln-acid plant and developed a process that is said to enable H_2SO_4 and high-quality cement to be made from by-product gypsum. In a large scale demonstration in 1967, one of four kilns that normally run on anhydrite operated successfully on by-product gypsum. The efficiency of conversion of $CaSO_4$ in the by-product gypsum to H_2SO_4 is 80 per cent and the ratio clinker to H_2SO_4 about 0.93. No special quality or type of by-product gypsum is required because the process and equipment can be adapted to accommodate different types of by-product gypsum, but it is interesting to note that the "guide analysis" for by-product gypsum shows its P_2O_5 content as less than 1 per cent and F as less than 0.3 per cent. It has not been stated how the effect of P_2O_5 or CaF_2 on clinker quality is overcome. This is obviously part of the know-how which operators are unwilling to disclose.

The key to the successful operation of the process is said to be in the control of the kiln operating conditions because by-product gypsum is more reactive than mineral calcium sulphates. The amount of coke in raw meal and the air added to oxidize sulphur have to be adjusted accordingly. Control of raw meal composition and kiln operating conditions are thus even more important when using by-product gypsum than when working with mineral calcium sulphate.

It is reported that plans are in hand in Coswig to construct a kiln-acid plant to operate solely on by-product gypsum. This would be an important development because the ultimate test of the use of by-product gypsum in a kiln-acid plant is continuous operation with production of high-quality clinker.

V. E. B. Chemie-Ingenieurbau, Leipzig, German Democratic Republic, is prepared to design, construct and commission kiln-acid plant working on by-product gypsum (see "Know-how on the process for the simultaneous production of SO_2-containing gases and cement on the basis of phosphoric acid gypsum" by V. E. B. Chemiewerk, Coswig, and *Sulphur* [1968] No. 74).

Marchon, and their engineering contractors Power-Gas, have also been working on the use of by-product gypsum. The scale of this work is not stated, but it has permitted them to offer kiln-acid plants utilizing this material. They are unwilling to disclose information on their work (Paper to Fertiliser Round Table, Washington, D. C. November, 1966), but it has been stated that their process can use by-product gypsum containing up to 0.5 per cent P_2O_5 and that laboratory tests can predict commercial performance at higher P_2O_5 contents (*Chemical Week*, 1968).

Österreichische Stickstoffwerke AG have also investigated the use of by-product gypsum in kiln-acid plants and their contractors will quote for such plants using by-product gypsum but details of these investigations do not seem to have been published.

Effect of the use of by-product gypsum on the capital and operating costs

Capital costs

Plant for the dehydration of by-product gypsum may be a little less expensive than plant for the dehydration of natural gypsum which requires grinding before dehydration. The battery limit costs given in Section D of chapter 3 should be increased by 8 — 10 per cent to obtain a preliminary estimate of the capital cost of a kiln-acid plant working on by-product gypsum. The higher fixed capital cost will also increase the working capital.

Operating costs

The only significant addition to the operating cost of a kiln-acid plant when anhydrite is replaced with by-product gypsum, apart from those costs expressed as a percentage of the total fixed capital, is the cost of dehydrating the gypsum. The fuel requirement will depend on the free water content of the by-product gypsum and the thermal efficiency of the dehydration equipment used. Figures quoted by contractors (assuming that fuel oil has a calorific value of 10,000 t cal/ton) vary between 1,000 and 1,600 t cal of additional heat per ton of H_2SO_4 when by-product gypsum is used. For preliminary evaluation, an additional heat requirement of 1,500 t cal per ton of H_2SO_4 should be used. A more accurate heat requirement can be calculated when the free water content of the by-product gypsum is known.

In addition to the fuel cost, electricity, water and process operating labour must be added to obtain the plant cost of dehydrated gypsum, less maintenance which is covered as a percentage of the capital cost. The electricity and water requirements can only be guesses at this stage, but it is suggested that 50 kWh and 20m^3 per ton of dried gypsum be taken for preliminary evaluation. It can also be assumed that the plant would require one man per shift in developed countries.

An approximate plant cost, less maintenance, of dehydrated gypsum can be calculated from these figures. To a first approximation, the plant cost of dehydrated gypsum, less maintenance, is unlikely to differ appreciably from the cost of anhydrite if this is won where the acid is made and both are expressed as £/ton of H_2SO_4.

If, as has been suggested at the Fertiliser Round Table in November 1968, it may on occasion be desirable to put by-product gypsum to an intermediate stockpile, the cost of by-product gypsum may be greater than that of anhydrite, but if anhydrite incurs appreciable carriage charges, it will certainly be more costly than by-product gypsum.

D. SUMMARY

The anhydrite kiln process has been adapted for the production of SO_2-containing gas and Portland cement clinker from gypsum made as a by-product of phosphoric acid manufacture. Some of the fluorine present in the by-product gypsum enters the SO_2-containing gas, but this fluorine which would poison the vanadium oxidation catalyst, can be removed during the gas cleaning operations and there are therefore no problems in the use of this gas for sulphuric acid manufacture. The limits of impurities, especially P_2O_5 and F in by-product gypsum, for the production of high-quality cement are not given in the literature, but published information suggests that cement can be made which meets BS 12:1958, but leaves it uncertain whether this cement would satisfy those users for whom high-early strength is needed. A potential user of by-product gypsum in a kiln-acid plant should ascertain the uses to which the cement would be put and obtain explicit guarantees that the cement made from by-product gypsum would meet requirements.

E. POSSIBLE EFFECTS OF THE USE OF BY-PRODUCT GYPSUM IN THE KILN-ACID PROCESS ON THE OPERATION OF THE PHOSPHORIC ACID PLANT

Gypsum produced as a by-product of phosphoric acid manufacture is usually dumped. The composition of the gypsum is therefore of little importance to the operator of a phosphoric acid plant, although he will usually wish to minimize the P_2O_5 lost in it. There may, however, be occasions when he is prepared to accept a higher P_2O_5 loss in the gypsum, for example, to increase phosphoric acid output. If the by-product gypsum is to be fed to a kiln-acid plant, the phosphoric acid plant operator will have to produce his by-product gypsum to a specification and this may interfere with the way in which he would otherwise wish to run the phosphoric acid plant.

If gypsum is to be produced to a specification in a new phosphoric acid plant, the plant should be carefully designed to convert as much as possible of the P_2O_5 in the phosphate rock into water-soluble P_2O_5, this minimizing the water-insoluble P_2O_5 in the gypsum. The amount of water-soluble P_2O_5 in the gypsum will depend on the washing efficiency of the gypsum filters. These also determine the free moisture content of the gypsum. The filters should therefore be chosen to produce a gypsum filter cake with the minimum practicable amount of water-soluble P_2O_5 and the lowest possible free water content.

The gypsum specification may also limit the F content. This will vary with the type of phosphate rock used. For example, a rock high in SiO_2 and F will produce fluosilicic acid and/or its sodium salt if sodium is present in the rock. All the fluosilicic acid and the sodium fluosilicate up to the limit of its solubility will go out in the phosphoric acid, giving gypsum which is relatively low in F. On the other hand, phosphate rock high in F, but low in SiO_2 will produce gypsum with a relatively high F content. The purchaser of a phosphoric acid plant should ascertain if his choice of phosphate rocks is likely to be restricted by the specified F content of the by-product gypsum because he might find such a restriction to be commercially undesirable.

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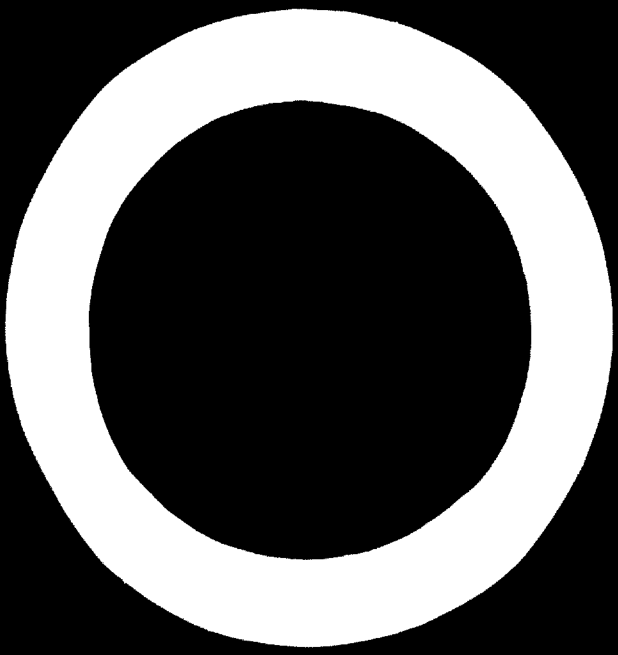

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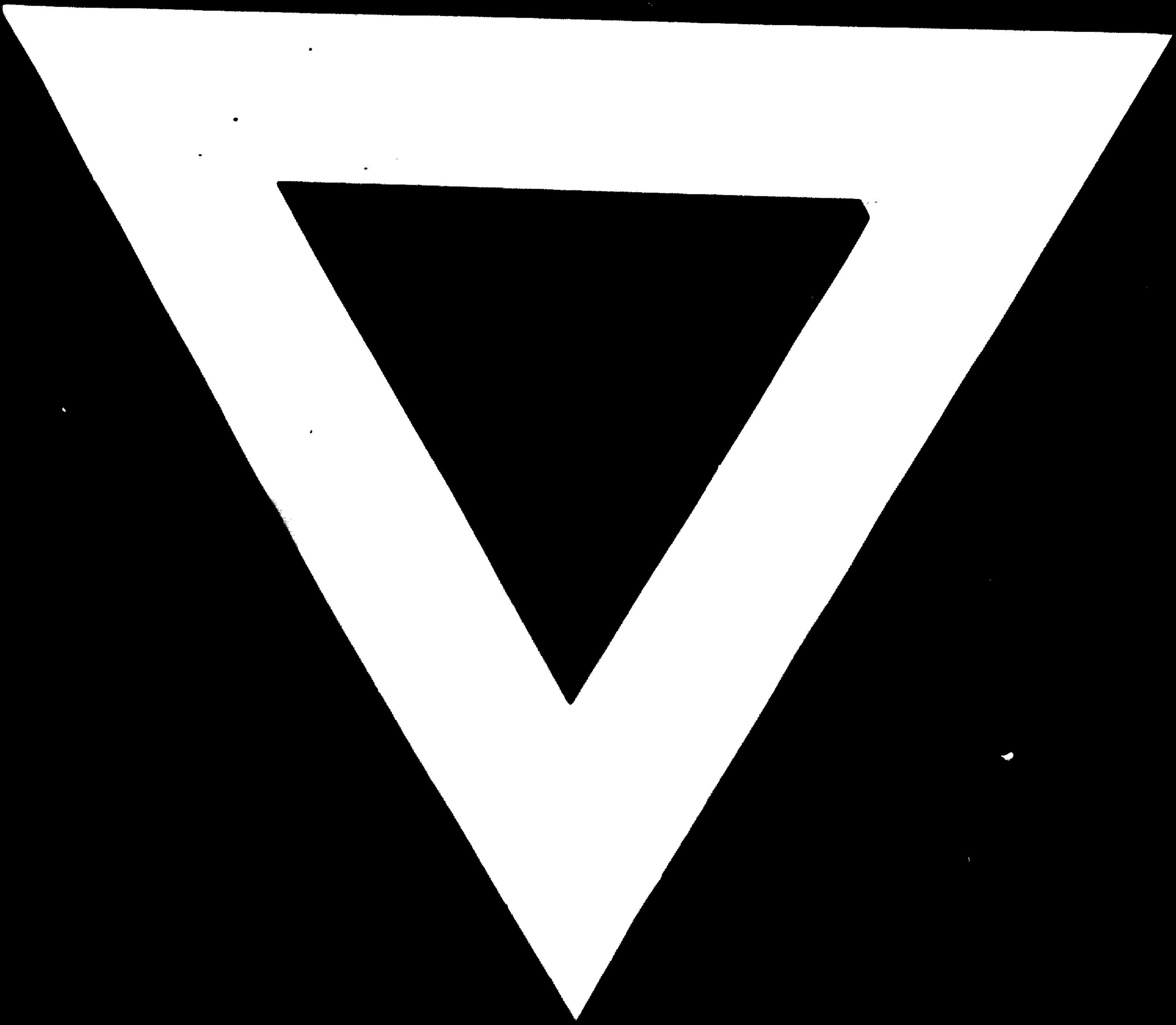

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