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(Geol. Ser. No. 27)

THE PRODUCTION OF SULPHURIC ACID AND
PORTLAND CEMENT FROM CALCIUM SULPHATE AND
ALUMINIUM SILICATES.

THE CHEMICAL FUNDAMENTALS.

by

E.K. Sturmfels

CANBERRA, A.C.T.

16th June, 1949.

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1. S U M M A R Y

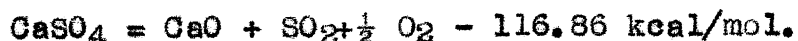
Sulphuric acid may be produced not only from sulphides but also from calcium sulphate, by the use of which portland cement can be manufactured simultaneously with the acid. For the manufacture of sulphuric acid and portland cement from calcium sulphate and aluminium silicates, a mixture of anhydrite, clay, sand, and coke as a reducing agent, is usually used.

However, it is possible to use gypsum instead of anhydrite and oil shales or other fuels instead of coke. Furthermore, it is not always necessary to add the aluminium silicates separately; they may be contained as impurities in the anhydrite or gypsum rocks, or in the ash of the coke or oil shales. Hence, it is quite possible to obtain a portland cement clinker conforming to the customary standards without adding clay or sand, provided that the non-volatile components of the raw materials already have the correct composition.

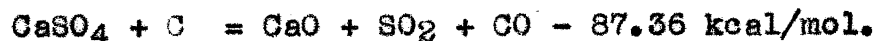
2. REACTIONS INVOLVED IN THE PRODUCTION OF SULPHURIC ACID AND CEMENT FROM CALCIUM SULPHATE

The fundamental idea when using calcium sulphate instead of sulphides for the manufacture of sulphuric acid is to produce in one single process not only sulphur dioxide but also portland cement clinker by burning an appropriate mixture in a rotary kiln. The sulphur dioxide can be converted in the usual manner by the contact process.

The complete thermal decomposition of calcium sulphate without reducing medium is possible only above 1375° C :



By adding a reducing agent like coke to fix the generated oxygen, the reaction starts at lower temperatures and needs less energy :



By further reaction between CaSO_4 and CO , CO_2 may be generated.

Besides the reactions shown above, the calcium sulphate can be reduced to calcium sulphide by too high a proportion of coke :



Too rapid a reduction should be avoided; otherwise, a large quantity of calcium sulphide would be produced causing the mass in the kiln to fuse instead of sinter and the calcium sulphide itself to enter the cement clinker to a high percentage. Hence, less than 1 mol C (from the reducing coke) for every mol CaSO_4 should be used.

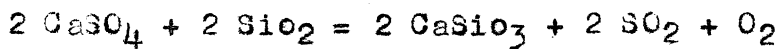
A method of avoiding premature action of oxygen and the formation of calcium sulphide, developed by G. Polysius A.G., Dessau, Germany, consists of forming granules from the mixture of gypsum, clay and carbon. These granules have a size of 3 to 20 mm diameter and are prepared by adding water to the pulverized mixture⁽¹⁾.

(1) British patent No. 326,612. Accepted March 20th, 1930.

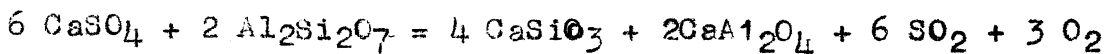
In the process of decomposition of CaSO_4 , the basic sulphate $\text{CaSO}_4 \cdot \text{CaO}$ may be partly formed, according to P.B. Budnikoff (2), because its fusion temperature is much lower than the temperature of dissociation of gypsum. This may sometimes lead to the fusion of the mass instead of its sintering and to a surplus of calcium sulphate in the cement clinker.

Aluminium silicates, for instance clay and sand, have to be part of the charge, not only to obtain cement clinker but also to accelerate the process of decomposition of the calcium sulphate by fixing calcium oxide, transforming it into calcium silicates and calcium aluminates, and so removing it from the process.

According to Budnikoff (3), at 1273°C the following reaction between calcium sulphate and silica takes place :

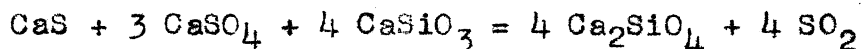


With aluminium silicate, calcium sulphate reacts at 1130°C :

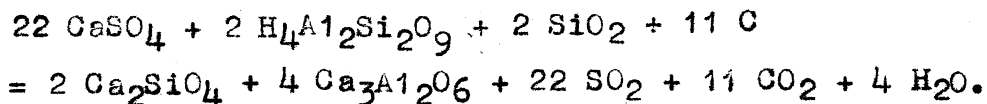


By further burning in the furnace, di-calcium silicate, tri-calcium silicate and tri-calcium aluminate are produced instead of mono-calcium silicate and mono-calcium aluminate.

If calcium sulphide has been formed from calcium sulphate, it can also react with calcium silicate :



Summarizing, the entire reaction between calcium sulphate, aluminium silicates, and a reducing agent like coke may be represented by the following equation :



Other elements which are usually contained in the raw materials used in this process, like sodium, potassium, magnesium, and titanium, have no influence on the above reactions. Only the presence of larger amounts of iron oxide may be of importance since iron oxide can combine with calcium oxide and aluminium oxide to form $\text{Ca}_4\text{AlFe}_2\text{O}_{10}$.

By fractional burning, fusion of the charge may be avoided and the proportion of calcium sulphate in the clinker lowered, according to Budnikoff (4). In order to lengthen the time during which the mass remains in the zone of maximum dissociation of CaSO_4 , he suggests that the process be conducted preferably in a rotary kiln with 'enlarged zone'.

(2) Budnikoff, P.B., 1935: Portland cement and sulphuric acid from gypsum anhydrite. Concrete (mill. sect.), Vol. 43.

(3) l.c.

(4) l.c.

3. THE RAW MATERIALS FOR THE PRODUCTION OF SULPHURIC ACID AND CEMENT FROM CALCIUM SULPHATE.

31. Anhydrite and Gypsum.

For the production of sulphuric acid and cement from calcium sulphate, anhydrite which contains no water is usually used, and not the hydrated gypsum.

However, it is quite possible to use gypsum instead of anhydrite. Of course, by introducing a large amount of water which has to be vaporized in some way, the costs of the process will be raised to a certain degree.

There are two possibilities : either dehydrating the gypsum by a special operation before mixing it with the other ground materials; or, provided that the gypsum does not contain much uncombined water, grinding the raw gypsum as it is worked and mixing it with the other parts of the charge before burning in the kiln. In this second case, more fuel will be required for the burning process in order to evaporate the combined water of the gypsum, and the concentration of sulphur dioxide in the gases leaving the furnace will be less, but a costly separate treatment of the raw gypsum can be avoided.

The gases leaving the kiln contain nitrogen and sulphur dioxide as main constituents. Using raw materials which contained no carbonates, only 2.6% H₂O, and 45.2% SO₂, a German plant found some years ago 8.8 per cent by volume of SO₂ in the gases. If nearly pure gypsum rock were used instead of anhydrite, the content of SO₂ in the gases would drop to about 7 per cent.

Since the sulphur di-oxide has to be oxidized to sulphur tri-oxide by the contact process, the gases leaving the kiln must be mixed with air. Thus, if nearly pure anhydrite is used, the proportion of SO₂ in the gases will be lowered to about 5 per cent by volume, and, if using gypsum rocks, to about 4.5 per cent. To-day, however, sulphuric acid can easily be generated from gases containing 4.5 or 5 per cent by volume of SO₂ by the contact process.

It is by no means necessary that the anhydrite or gypsum rocks be especially pure; impure anhydrite or gypsum deposits can be used as well for this process. Impurities which are contained in these rocks, so far as they are not volatile, enter the cement clinker. By choosing suitable parts of the anhydrite or gypsum deposits which are to be worked, it is often possible to recover a raw material which already contains all the constituents of a portland cement in the correct proportions, so that no clay and sand have to be added.

It is essential that the impure anhydrite or gypsum rocks do not contain too much carbonate, especially not too much calcium carbonate; the amount of calcium carbonate should be less than 5%, otherwise the quantity of cement clinker produced would become too large compared with the amount of sulphuric acid generated.

32. Coke and Oil Shales as Reducing Agents.

As the reducing agent, coke is usually used. Nevertheless, it is possible to substitute other materials, for instance coal or fuel oils. As far as the limited information available indicates, oil shales probably can be employed for this purpose.

There exists a Canadian patent according to which oil shales may be used to reduce calcium sulphate and generate sulphuric acid⁽⁵⁾. The patent claims protection essentially for the following process: mixing dried and pulverized anhydrite with pulverized oil-yielding shale fines or retorted oil yielding shale; burning the mixture either without adding anything else by spraying fuel oil on it, or by intensifying the heat during operation in another way; and finally recovering the gases evolved and converting them into sulphuric acid in the usual manner.

The description of this process is quite obscure, probably on purpose. However, it indicates that it is possible to use oil shales to reduce calcium sulphate. It is not known which of the above mentioned various methods included in the patent have actually been proved and used on an industrial scale.

Attention should be paid to the fact that large amounts of non-volatile components would be introduced into the charge by the oil shales. It is necessary that these non-volatile oil-shale components which consist mainly of aluminium silicates correspond, together with the other non-volatile components of the charge, with the standard composition of portland cement. The amount of calcium oxide in the oil shales not present as calcium sulphate should be low; otherwise too much cement clinker would be produced compared with the amount of sulphur dioxide generated.

33. The Fuel Consumption.

To burn the mixture in the rotary kiln, comparatively low-grade fuels like black coal fines, brown coal, or fuel oils, may be used as long as it is possible to obtain a temperature of about 1400° C which will be required to form portland cement clinker.

For the production of 1 kg cement clinker and the corresponding amount of sulphur dioxide the following quantities of fuel for reducing and burning are needed, according to Budnikoff⁽⁶⁾ provided that more or less pure anhydrite rocks are used:

Coke consumption for reduction	0.135 kg
Coal consumption for the rotary kiln	0.242 kg
Total consumption	0.377 kg

(5) Canadian patent No. 308,293, issued 3rd February, 1931, for Louis Simpson, Albert Mines, New Brunswick, Canada.

(6) l.c.

Budnikoff(7) gives the following heat balance sheet for the process:-

<u>Gain of heat</u>		<u>Consumption of heat</u>	
From burning of fuel	67.6%	For vaporization of moisture	4.4%
Heat of formation of CO ₂ from CO	31.4	For removal of water of hydration	0.6
Other sources	1.0	For dissociation of CaSO ₄	37.6
		Carried off with kiln exit gases (750°C)	34.3
		Overheating of water vapor	2.3
		Carried out by clinker (100° C)	0.6
		Losses through convection and radiation	19.4
		Other losses	0.8

The same author calculates from this heat balance that the theoretical consumption of heat for the production of 1 kg of clinker and the corresponding quantity of sulphur dioxide is 2521 kcal, including the inevitable losses of heat.

P. Parrish(8) reports that considerably larger quantities of fuel were needed in England for the production of 1 kg of clinker, obviously by employing wet raw materials :

Ordinary coal for drying of raw materials	0.17 kg
Low grade coke fines for reduction	0.37 kg
Coal dust for the rotary kiln	0.28 kg

Total consumption 0.28 kg

In Germany, some years ago, the following quantities of fuel were used for the production of sulphuric acid and portland cement clinker from anhydrite, clay, sand, and coke, the figures applying to the manufacture of 1 kg of cement clinker:-

Coke fines for reduction (70% C, 12% ash, about 6500 kcal/kg)	0.14 kg = about 900 kcal
Brown coal dust for burning (55% C, 11% ash, about 5000 kcal/kg)	0.36 kg = about 1800 kcal
Total consumption	0.50 kg = about 2700 kcal

This figure of 2700 kcal corresponds very well with the theoretical consumption of 2521 kcal, given by Budnikoff(9). More energy would be needed, of course, if lower grade raw materials were used, for instance gypsum rocks instead of anhydrite or oil shale instead of coke.

(7) l.c.

(8) Parrish, P., 1929: The significance of the production of sulphuric acid from anhydrite. Industr. Chemist, Vol.5 pp.491-493.

(9) l.c.

34. The non-volatile components as source of the formation of cement clinker.

As stated above, aluminium silicates are required for the process; they can either be present as impurities in the anhydrite or gypsum rocks; or they may partly be contained in the ashes of coke, coal, or oil shale, whichever is used as reducing agent; or they have to be added to the charge as clay and sand. In certain variants of the process even the ash of the fuel used for the heating of the rotary kiln may become part of the cement clinker.

The non-volatile components of the mixture used for the process consist mainly of calcium oxide, silicon dioxide, and aluminium oxide, together with smaller amounts of iron oxide, magnesium oxide, alkali oxides, and titanium dioxide. These non-volatile components pass over into the cement clinker, mostly with a small amount of undecomposed calcium sulphate. In order that a satisfactory portland cement may be produced, certain standards have to be met.

Usually, the properties of a portland cement are not given by the percentage of its chemical composition, but by certain ratios showing the relations between the different components. The alumina ratio gives the proportion of aluminium oxide to iron oxide, and the silica ratio, the proportion of silicon dioxide to aluminium oxide plus iron oxide. More important than these two ratios, which may vary between wide limits, are the hydraulic ratio and the lime standard. The hydraulic ratio indicates the proportion of calcium oxide to silicon dioxide plus aluminium oxide plus iron oxide; this ratio should be between 2.0 and 2.3. The lime standard shows the percentage of calcium oxide available to fix the other components of the charge; it should amount to 96 to 99%; a lime standard of more than 100% means that there exists free calcium oxide which would considerably lower the quality of the cement and cause excessive expansion of the concrete.

These different ratios are summarized in the following table:-

	Formula	Favourable values for portland cement.
Alumina ratio	$\frac{Al_2O_3}{Fe_2O_3}$	More than 1.0
Silica ratio	$\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$	1.8 - 3.5
Hydraulic ratio	$\frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3}$	2.0 - 2.3
Lime standard	$\frac{100 CaO}{2.8 SiO_2 + 1.18 Al_2O_3 + 0.65 Fe_2O_3}$	96 - 99%

There remain some other conditions with which a portland cement should comply (10). A high grade cement should contain a large proportion of tri-calcium silicate (Ca_3SiO_5), about 40 to 50%; on the other hand the content of alumina and

(10) United States, Department of the Interior, Bureau of Reclamation, 1941: Concrete Manual. 3rd edition.

consequently of tri-calcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$) should be comparatively low as many undesirable properties of cements are due to too high a percentage of tri-calcium aluminate.

A limited quantity of iron oxide may be useful for fixing aluminium oxide as $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ which supersedes the inferior tri-calcium aluminate. However, the amount of iron oxide should not exceed that of aluminium oxide; otherwise, the detrimental di-calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) would be formed.

The proportion of the magnesium oxide present should be less than 4% of the non-volatile components, and the cement clinker must contain not more than 2.75% sulphur tri-oxide after burning⁽¹¹⁾.

(12) (13) As shown recently by Alderman, Gaskin, Jones, and Vivian . even less than 1% of alkali oxides (sodium and potassium oxides) within the cement may be very dangerous in the mortar. If there is any cryptocrystalline quartz or opal present in the aggregate used for the mortar, even small amounts of alkali oxides tend to combine with it and to cause excessive expansion; and in the hardened mortar, alkali oxides can still migrate and cause damage. However, since a large proportion of alkali oxides contained in the charge will be volatilized in the kiln, the raw materials may contain up to 1% alkali oxides.

(11) Standards Association of Australia, 1939 : Australian standard specification and methods of test for portland cement and high early strength portland cement. Standards Assoc. Aust. Technical Standard No. A 2 - 1939.

(12) Aldermann, A.R., Gaskin, A.J., Jones, R.H., and Vivian, H.E. 1947: Australian aggregates and cements. Studies in cement-aggregate reaction. Coun. Sci. Ind. Res. (Aust.) Bull. No. 229, pp.7-46.

(13) Vivian, H.E., 1947: The effect of alkali movement in hardened mortar. Studies in cement-aggregate reaction. Coun. Sci. Ind. Res. (Aust.) Bull. No. 229, pp. 47-54.