

Kinetics and mechanism of sulfation reactions during roasting of sulfides

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ROASTING of sulphidic minerals is one of the very important steps in the extraction metallurgical practice of most of the non-ferrous metals from their concentrates. In recent times, the technique of roasting has undergone substantial changes leading to higher production and better products, more suitable for subsequent operations. Some of these processes have developed on the basis of our understanding of the kinetic limitations of the old processes and elimination of such kinetic bottlenecks like diffusion in the roasting processes. These new processes like flash roasting or fluidized roasting are being increasingly utilised in production units. However, our present state of knowledge on the kinetics of roasting reaction lacks certain fundamental understanding of the process which is explained in the following paragraphs.

The mechanism of roasting of sulphides has been the subject of a large number of research papers contributed by Soviet scientists, reviewed by G. S. Frents,¹ Wadsworth^{2,3}, McCabe⁴, Alcock⁵ have advanced the knowledge of roasting processes to a large extent. What emerges out of these investigations can be summarized as follows:

- (a) Roasting of a sulphide, depending on temperature of roasting and ambient sulphur trioxide partial pressure, can give rise to oxide of metal, or sulfate of metal or basic sulfate.
- (b) The formation of metal oxide at sufficiently high temperature is a direct result of the roasting process.
- (c) Formation of metal sulfate can be either due to direct conversion of metal sulphide to sulfate or first the metal sulfide gets oxidized to metal oxide, which acts as a catalyst⁸ for the formation of SO_3 from SO_2 and O_2 , and then this SO_3 reacts with oxide to give sulphate.

While the above work has given substantial and significant data yet a definite mechanism of roasting cannot be derived from it as many questions still remain unanswered. Some of the most important questions are:

SYNOPSIS

The present study on the formation of sulfates of zinc and nickel from their oxide, shows that the sulfation process involves formation of sulphur trioxide from sulphur dioxide and oxygen, and subsequent reaction leads to formation of sulfates. The sulfation rate is highly dependent on the defect structure of the oxides; it was observed to be very high in case of nickel oxide and almost negligible in the case of aluminium oxide.

In the above studies powdered samples have been used and the reaction rate seems to be activation controlled.

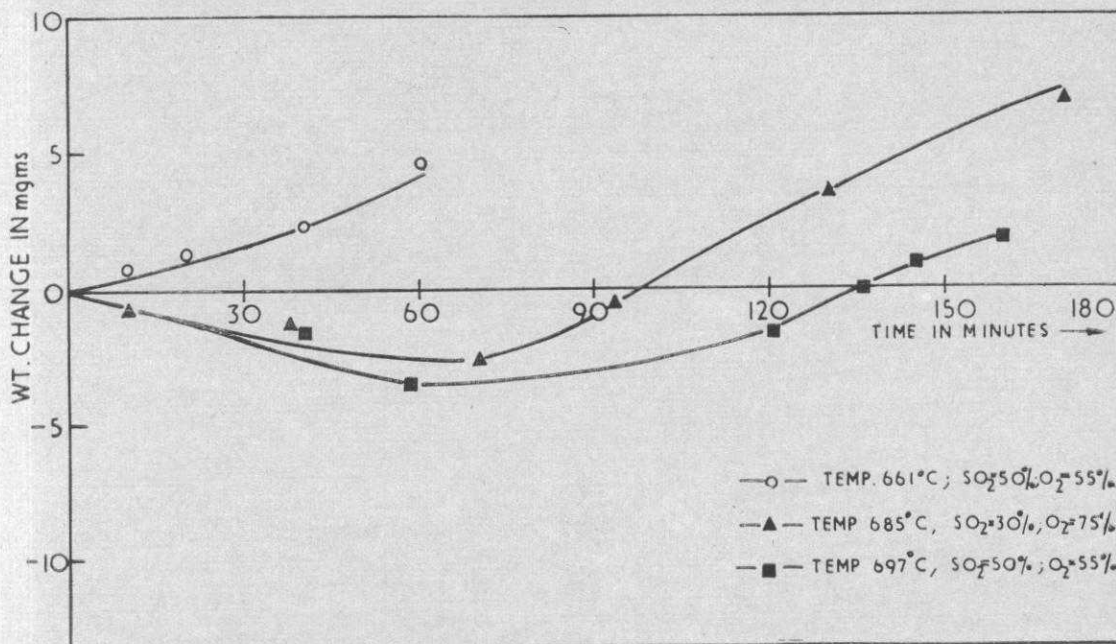
- (a) Will metallic sulfides of different metals show the same type of mechanism for sulfation as well as oxide formation?
- (b) Will not the nature of the metallic sulfide or oxide produced influence the subsequent product formation?
- (c) Has the electron defects of sulphide or oxide any role to play in the roasting process so far as kinetics of the process are concerned?

In the present investigation only the sulfation mechanism has been investigated, and the findings clearly point out the role of defect structure in the roasting mechanism.

Experimental set-up

The kinetics of the sulfation of zinc oxide (B. D. H. Analar Quality) and nickel oxide (Russian grade Analar Quality) were studied by gravimetric technique. A spring of high carbon steel wire with accuracy well within 0.2 mg was used for measuring weight change. The sample was taken in a pyrex glass bucket, hanging freely inside a pyrex glass tube reactor, with a gold wire attached to the spring; the reactor being surrounded by a double wound type movable furnace with a temperature control within $\pm 5^\circ C$. Flow of O_2 and SO_2 were measured through calibrated flow-meters and the mixture dried by bubbling through concentrated sulfu-

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1 Weight change vs time relationship for the sulfation of zinc-sulfide, under different atmospheres and at different temperatures

ric acid and then passing it through a tower of drierite.

Samples

Mixtures of zinc oxide and lithium sulphate and of nickel oxide and lithium sulphate were prepared by mixing powdered sample of dried lithium sulfate of requisite quantity with zinc oxide or nickel oxide and

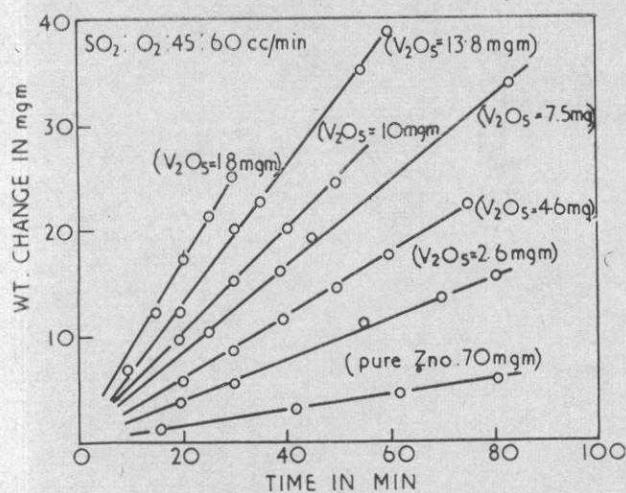
then heating the mixture in a muffle furnace to a temperature of 930°C for 90 minutes, in case of zinc-oxide and at 660°C for 6½ hrs for nickel oxide. The zinc sulphide used was RIEDEL make and was dried at 200°C before use.

Results and discussion

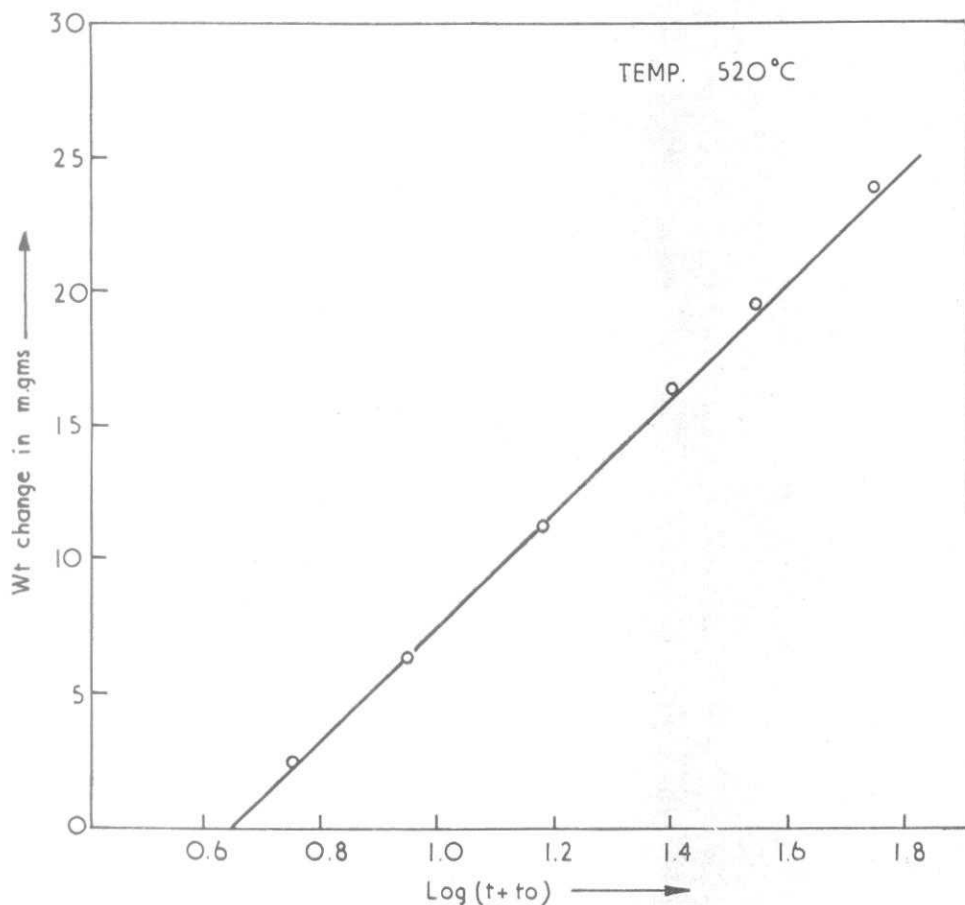
Fig. 1 shows the variation of weight with time for zinc sulfide sample. It is evident that there is a fall in weight for certain length of time followed by a rise indicating formation of zinc oxide and subsequent conversion to zinc sulfate. The falling part corresponds to zinc oxide formation as well as conversion to zinc sulphate, the amount of zinc sulfate formed being low due to low amount of zinc oxide formed leading to loss of weight; the rising part represents loss in weight as well as gain in weight due to simultaneous formation of zinc oxide and zinc sulfate, the second reaction superseding the first one due to the presence of sufficient zinc oxide in the system.

Fig. 2 gives the weight change vs time relation for the formation of zinc sulfate from zinc oxide. This rate, as shown by the authors, can be accelerated by addition of vanadium pentoxide to the system. Vanadium pentoxide is well known as a catalyst for the formation of SO_3 from SO_2 and O_2 and as such it proves that SO_3 formation is the most critical step in the sulfation reaction of zinc oxide.

Fig. 3 shows the rate of formation of nickel sulfate from nickel oxide, which shows an Elovich type of equation in contrast to zinc oxide where a linear variation was observed.



2 Weight change vs time relation for pure ZnO and ZnO+V₂O₅ mixtures at 625°C



3 Exponential kinetics followed in the sulfation of nickel oxides

Apparent activation energy measure for zinc oxide doped with lithium sulfate and nickel oxide with lithium sulfate indicates a rise in activation energy. In case of zinc oxide it changes from a value of 16 Kcal/mole to 24 Kcal/mole, and in case of pure nickel oxide from 12 Kcal/mole to 19 Kcal/mole in case of nickel oxide doped with lithium sulfate.⁶

It has also been observed that aluminium oxide cannot be converted to its sulfate under identical conditions even in the presence of vanadium pentoxide. The effect of vanadium pentoxide was also observed to be negligible on the sulfation of nickel oxide.

From the above observations, the following conclusions can be drawn :

- (i) In case of zinc sulfide, the formation of zinc sulfate always takes place through the formation of zinc oxide at least within the range of temperature studied here.
- (ii) Formation of zinc sulfate from zinc oxide + SO₂ and O₂ mixture by itself a slow process, can be enhanced by addition of V₂O₅ to the system.
- (iii) Nickel oxide shows a much more rapid sulphating characteristic although the rate laws followed by zinc oxide and nickel oxide are different.

It is apparent from these observations that sulfating theory as proposed by Wadsworth *et al.*²¹ is valid and zinc oxide or nickel oxide catalyses the formation of SO₃ from SO₂ and O₂, which reacts with zinc oxide/nickel oxide to produce zinc sulfate/nickel sulfate.

However, the first question which arises is whether SO₃ is formed *insitu* or reacts from the gas phase.

The authors' observations have shown⁷ that in the plot of rate of sulfation of zinc oxide vs amount of V₂O₅ addition to it, at a fixed temperature, SO₂/O₂ ratio gives a straight line which when extrapolated back to zero V₂O₅ addition cuts the rate axis at a rate which is that of pure zinc oxide under similar temperature and SO₂/O₂ ratio. Since V₂O₅ is a known catalyst for formation of SO₃ from SO₂+O₂, SO₃ from gaseous phase can be taken to react with zinc oxide to give zinc sulfate. The formation of zinc sulfate in the absence of V₂O₅ however may be assumed to take place from the surface adsorbed state.

In the case of nickel oxide, no enhancement of rate is being observed with addition of V₂O₅ and aluminium oxide does not give any sulfate under identical conditions.

The next question which arises is that in case of

zinc oxide a direct reaction with SO_3 is possible whereas such a reaction is impossible for nickel oxide.

The above two observations cannot be answered without due consideration of the peculiar properties of these oxides. Zinc oxide is known to be an n-type oxide i.e., having excess Zn^{2+} ions trapped interstitially along with e^- (electrons) in such a quantitative relationship as $e^+ e^- = \text{constant}$, these e^- (trapped) electrons providing for the semi-conducting property of the oxide. Nickel oxide on the other hand a p-type oxide, has positive holes (e^+) in large excess and few trapped electrons. Al_2O_3 is more or less a perfect lattice with no trapped electrons of positive holes, hence, its name 'insulator'.

All catalytic reactions are essentially the result of adsorption process. The SO_2 , O_2 both might be adsorbed on the oxides or only one may be adsorbed and the other may react from the gas phase.

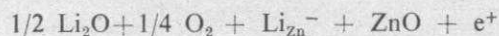
On zinc oxide and nickel oxide, adsorption of oxygen takes place and attains equilibrium as has been shown by Wagner.^{8,9} For the adsorption electron donation takes place from the substrate to O_2 as O_2^{2-} or O^{2-} . Zinc oxide which possesses excess electrons, donates the electron for the adsorption, and nickel oxide donates and thereby increases hole concentration. Aluminium oxide has no capacity or has poor capacity to donate electrons and therefore the adsorption is not possible and $\text{SO}_2 \rightarrow \text{SO}_3$ conversion is not possible.

Since oxygen adsorption goes to equilibrium, the adsorption of SO_2 may be the rate controlling step and assuming SO_2 to SO_2^{+} as the adsorption species one can imagine that the process of electron donation to the zinc oxide will be more hindered than in the case of nickel oxide, where electron concentration is very small to start with. Therefore nickel oxide should act as a catalyst in a better way than zinc oxide, which explains the question.

The question why SO_3 adsorbs better on zinc oxide than nickel oxide can be explained on similar assumption as when SO_3 will adsorb, it will do so as SO_3^- , that is by extracting electron from the substrate, which only zinc oxide is capable of.

To further examine the process a series of studies were made with lithiated ZnO and nickel oxide. In each case the activation energy was found to increase.

When lithium dissolves in ZnO, it acts as an acceptor, according to the reaction



This substitution of lithium on zinc sites in ZnO tends to increase the hole concentration in the valence

band, which means a decrease of electrons (e^-) in the valence band, since there is the following relation between holes and electrons.

$$K = e^- \cdot e^+$$

Now, if less electrons are available in the conduction band for adsorption, reaction involves deeper level electrons, hence higher energy is required, which resulted in increase of activation energy for sulfation of ZnO doped with lithium sulfate.

The rise of activation energy for sulfation of nickel oxide doped with lithium sulfate can be explained similarly. On adding Li_2SO_4 to nickel oxide, lithium dissolves substitutionally on the nickel sublattice as a monovalent ion Li^+ . Since Li^+ is substituting for Ni^{2+} , a positive charge is lost for each Li^+ ion added.

Now, to maintain the electroneutrality for each Li^+ introduced, a Ni^{2+} ion must be oxidized to the Ni^{3+} state, which virtually means from the ionization equilibrium:

$\text{Ni}^{3+} \rightleftharpoons \text{Ni}^{2+} + e^+$, that e^+ concentration in the conduction band increases or e^- (electron) concentration decreases, because of the relationship already referred i.e. $e^+ \cdot e^- = K$, and hence, here also in the reaction, deeper level electrons are required, which means an increase in the activation energy.

Acknowledgement

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Discussions

Dr P. K. Jena (Banaras Hindu University) : The paper is very interesting from an academic point of view in understanding the mechanism of the process. May I request the authors to offer their comments on extrapolating the suggested mechanism to higher temperatures ?

I may also suggest that kinetic studies at higher temperatures using various partial pressures of SO_2 and O_2 may throw some more light in further clarifying the mechanism of the process.

Mr B. K. Dhindaw (Author) : Since the present interest was for the elucidation of sulfating mechanism, any study beyond the stability limit of these sulfates would introduce an extra parameter due to its decomposition. Such data will be even more complex to interpret especially when the kinetics and mechanism of sulfation itself is least understood. In this light we feel that studies at higher temperatures will not lead to any advantage for establishing the mechanism. For studying the oxidation roasting where the product is expected to be only metallic oxide, higher temperature data will be of interest and has been studied by us under limited conditions. Here, once again, one must be careful about the formation of basic sulfate which can bring in a lot of complications at a temperature not too high for sulfate decomposition.

Dr L. Wallace Coffey (Operation Hardrock, New Delhi) : The sulfation of aluminium from coal ash by H_2SO_4 vapour to form aluminium sulfate, followed by extraction and decomposition to regenerate $\text{SO}_3 + \text{H}_2\text{O}$ for recycle has been accomplished at Battelle Memorial Institute. Can you comment on this in the light of your observation of no sulfation of Al_2O_3 in your work ?

Mr B. K. Dhindaw (Author) : The sulfation of alumina was not observed at the temperatures we worked. It will be unfair to say that alumina is a defect-free oxide but its defect concentration depends on temperature and also on the surrounding gases, viz., water vapour, etc., as has been observed also. In this case, firstly the temperature of extraction is not known, but at high enough temperature if sufficient quantity of defects are produced in alumina, it may react with SO_3 to give sulfate. Moreover, due to the sulfuric acid vapours, presence of moisture may also increase the defect concentration. We observed increased rate of sulfation of ZnO in presence of moisture because of the above conditions.

Mr M. Totlani (Bhabha Atomic Research Centre, Bombay) : 1. I would like to know, whether the roasting of sulphides was carried out in fluidized bed or in a different way ?

2. Due to differences in the physico-chemical properties of various nickel oxides there are wide differences in their amenability to sulphation. I would like to know, if this has been observed by the authors in their studies.

Mr B. K. Dhindaw (Author) : 1. The roasting of sulfides was conducted in a flow system, i.e. the samples contained in a bucket were hanging freely in a stream of gas mixture. The details of the experimental system are given in the paper.

2. Nickel oxide used in these studies was ANALAR quality, used directly from the bottle. It is very likely that different samples prepared by various methods will show different rates due to differences in surface areas and defect concentrations.