

# Lime-concentrate roasting studies—effect of activated limestone

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## Abstract

The roasting in air of pellets consisting of copper–iron sulphides and limestone and activated limestone has been investigated to explore the possibility of developing a metal production process that eliminates sulphur dioxide gas emissions. The effects of pellet porosity, sulphide: limestone ratio, pellet sizes and temperature on reaction kinetics were investigated. Thermogravimetry was carried out under air atmosphere. The weight gain of pelletized samples was used to identify and study the phases present in the reaction products.

The experimental results indicated that at 500 °C using activated limestone, a completely reacted pellet can be produced in about 50 min with very low emissions of sulphur dioxide (more than 95% of sulphur capture).

*Keywords:* Sulphide ores; Reaction kinetics; Roasting; Extractive metallurgy; Surface modification

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## 1. Introduction

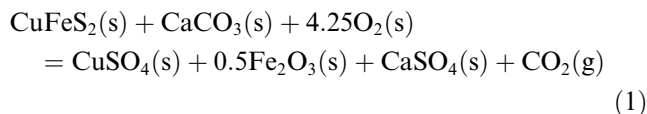
An alternative to conventional pyrometallurgical methods to solve the problem of high SO<sub>2</sub> emission is to use radically different process chemistry to permit the production of copper metal without SO<sub>2</sub> generation. One of these is based on the roasting of pellet of copper concentrate with lime as a reagent to absorb the sulphur and prevent the sulphur dioxide formation. This alternative technology was first described by Bartlett and Haung (1973, 1976) and Haver and Wong (1972, 1975), both of them using a mixture of chalcopyrite and hydrated lime at 500 °C. Terry et al. (1994a,b,c) carried out latest studies on the lime-concentrate roasting, oriented to have a better understanding on the optimum conditions of the process based on the extension of the study by Bartlett and Haung (1973, 1976). On the basis of the experimental results it was concluded that at 500 °C a completely reacted pellet of complex copper–iron sulphide with lime can be obtained in about 50 min. of reaction with very low emission of SO<sub>2</sub>. The reaction products are primarily CaSO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuSO<sub>4</sub> and CuO·CuSO<sub>4</sub>. A very high retention of sulphur was

found in the solid but with a rather low utilisation of the sorbent CaO (50%).

Following the observation that limestone reacts with SO<sub>2</sub> above 460 °C, a method of activation of CaCO<sub>3</sub> proposed by Calderbank (1979), tested in the removal of sulphur dioxide from the flue gas, was applied to the air roasting of copper sulphides. Those results are presented here.

## 2. Results and discussion

Prior to studying the effect of activated limestone, roasting experiments of mineral copper concentrate were carried out with additions of limestone under fixed experimental conditions based on the reports by Terry et al. (1994a,b,c). The sulphating reactions, assuming the production of copper sulphate, can be written as



From Eq. (1), the maximum theoretical weight gain expected is 12.5 wt%. Change on Gibbs free energy and enthalpy for this reaction are obtained from HSC software database:

$$\Delta G_{T(K)}^0 = 0.62 \cdot T(K) - 1614 \text{ [kJ/mole]} \quad (2)$$

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Table 1  
Experimental conditions and results for the oxidation and sulphation of copper concentrate-limestone pellets in air

Run	Temp. (°C)	Weight of pellet (g)	Porosity (%)	Reaction time (min)		Weight gain (g)	Weight SO <sub>2</sub> liberated (g)	Excess CaCO <sub>3</sub> (wt%)	Water added (wt%)	Pellet size <sup>a</sup> (mm)
				<i>t</i>	<i>t</i> <sup>*</sup>					
1	500	1.5842	36.8	80	40	0.1429	0.059	100	0	10
2	500	1.6915	32.9	95	40	0.1733	0.053	100	0	10
3	500	1.7841	28.9	110	50	0.1966	0.023	100	0	10
4	500	1.4824	35	90	30	0.0627	0.0713	68	5	10
5	500	1.4634	35	40	30	0.0432	0.0637	100	5	10
6	500	1.4209	35	35	30	0.0311	0.0311	200	5	10
7 <sup>b</sup>	500	1.4809	35	55	40	0.0795	0.0147	100	5	10
8 <sup>b</sup>	500	0.5830	35	50	35	0.0206	0.0098	100	5	7.5
9 <sup>b</sup>	500	2.8399	35	75	60	0.1774	0.0199	100	5	12.5
10 <sup>b</sup>	400	1.4717	35	75	70	0.0959	0.0275	100	5	10
11 <sup>b</sup>	600	1.4631	35	50	40	0.1300	0.0083	100	5	10

*t*, time from beginning of experiment; *t*<sup>\*</sup>, time when reaction ceases. Air flow rate: 360–370 cm<sup>3</sup> min<sup>-1</sup> (STP).

<sup>a</sup>All pellets are cylindrical and have diameter equals to their height.

<sup>b</sup>With activated limestone.

$$\Delta H_{T(K)}^0 = -1613.3 \text{ [kJ/mole]} \quad (3)$$

One of the advantages of adding limestone instead of lime directly with chalcopyrite is that the overall reaction is still exothermic, therefore the energy required in the production of lime from limestone is provided by the sulphide decomposition.

A series of runs using the same experimental apparatus and procedure as the one described by Terry et al. (1994a,b,c) were made at 500 °C with 1.0-cm diameter and 1.0-cm high pellets at different conditions and roasted in air. Table 1 gives the conditions and results of the thermogravimetric experiments.

By increasing the porosity, the sulphur retention and reaction rate decrease. By adding water the reaction rate seem to decrease, inhibiting the SO<sub>2</sub> capture by limestone. As the excess of limestone is increased, there is an increase in the reaction rate, but not benefit is observed on the sulphur retention.

Following the finding of Calderbank (1979), calcium carbonate was washed with a brine solution and then dried. It seems likely that the adsorption of traces of salt on the calcium carbonate alters the crystalline form of the ash formed at high temperature so that it became more permeable to SO<sub>2</sub> and CO<sub>2</sub>.

Fig. 1 illustrates the weight gain measured for copper concentrates with 100 wt% excess of activated limestone in pellet compared with those obtained at the same experimental conditions with dry and wet calcium carbonate (see Table 1). From here it is possible to observe that the reaction rate of copper concentrate with activated limestone is similar to that of wet calcium carbonate up to 25 min of reaction. In this point, the reaction rate of the latter decrease reaching a cessation point after 30 min of heat treatment. The reaction rate using activated limestone is much faster than with dry

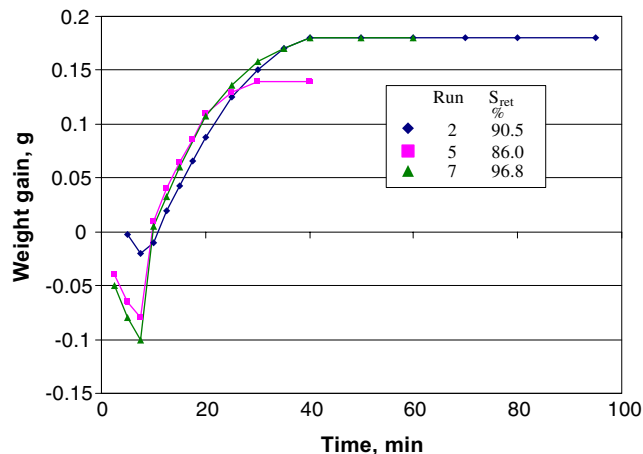


Fig. 1. Weight gain during roasting of copper concentrate-limestone at 500 °C with dry, wet and activated limestone. *S*<sub>ret</sub>, sulphur retained.

limestone, but both reach a cessation point at the same time (40 min). However, using activated limestone resulted in better sulphur retention, 96.8 wt% compared with 86.0 wt% for wet limestone or 90.5 wt% for dry limestone. These results indicate that activated limestone would be appropriate for the roasting of pellets of copper concentrates because excellent sulphur retention (>95%) is achieved.

To confirm the extent of reaction XRD analysis were undertaken on the roast product of run 7 before and after a leach test. The analysis of the calcine indicated the presence of Fe<sub>2</sub>O<sub>3</sub>, CaSO<sub>4</sub>, CuSO<sub>4</sub>, CaCO<sub>3</sub>; CuO·CuSO<sub>4</sub> and CuO. The XRD analysis of the leached and filtered residue showed the presence of Fe<sub>2</sub>O<sub>3</sub>, CaSO<sub>4</sub> and traces of CaSO<sub>4</sub>·0.5H<sub>2</sub>O, but did not show any line representing a copper compound. Analysis of

sample solutions by atomic absorption spectroscopy showed an increasing dissolution of copper throughout the test. It was found that in the final solution about 96% of copper was dissolved.

No effect on the reaction rate (on a relative mass gain basis) was observed by decreasing or increasing the pellet size, but the reaction time as well as sulphur retention increases with increase in size. No noticeable effect on reaction rate was observed by varying temperature. However, a better sulphur retention was observed at higher temperature. As pointed out by Terry et al. (1994a,b,c) it is undesirable to increase the temperature above 600 °C due to formation of cupric ferrites.

### 3. Conclusions

The principal conclusion that can be drawn from the work described here is that, by an appropriate selection of roasting conditions, pellets of copper concentrate and activated limestone can be roasted in air to give a completely roasted product in about 40–50 min with very low emission of SO<sub>2</sub> which is appropriate for recovering copper by further leaching.

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