Kinetics of copper segregation by the Torco process

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Discussion

Dr R. E. Robinson (Fellow): The author must be congratulated on a very meticulous and self-contained piece of work. It is indeed a pleasure to read a paper that is so clearly and systematically laid out, and where the conclusions and the testwork conducted have been so clearly described. The paper is complete in itself, which makes it very difficult for someone who is not intimately involved in the whole Torco project to make any comments on its content. However, two points that, strictly speaking, fall outside the scope of the paper are of considerable interest.

The first relates to the particle size of the material treated. In the paper, the testwork is confined to one standard particle size (minus 60 plus 100 mesh). The essential feature of the paper is to indicate that the rate-controlling reaction in the whole segregation process is the rate of reaction of the ore particles with the reducing agent and the hydrogen chloride. One wonders, therefore, to what extent this relatively slow rate of reaction is affected by the particle size of the ore itself. One imagines that the reaction must take place by contact of the hydrogen chloride with the surface of the mineral particles, and it is reasonable to suspect that the rate of diffusion of the copper ions to the surface is a relatively slow process and is thus the limiting factor in this particular rate of reaction. It is possible, for example, that the improvement obtained, when the ore is subjected to reducing conditions before the chlorination, is due to a breakdown in the crystal structure of the original particle. This breakdown is brought about by the reduction and by the consequent increase in surface area available for reaction with hydrogen chloride. Can the author indicate whether any work has been done along these lines, and whether it has been established that the reaction depends on the surface area available?

The second point relates to the application of this kinetic study to the actual operation of a Torco reactor. It was once planned to feed the sodium chloride, together with the reducing agent, into the top of the segregation chamber. In the paper, the author mentions that it has now been established that the segregation chamber behaves, to all intents and purposes, as a fluidized bed, and that there is, therefore, a rapid evolution of gas in the lower regions of the chamber, which, it is imagined, displaces the gas phase rapidly. Since the reaction between sodium chloride, water vapour, and the aluminium silicates in the ore is extremely rapid, one wonders how much of the hydrogen chloride produced is removed from the reaction zone before it has had time to react with the copper minerals.

The extremely low consumption of sodium chloride (which is a vital feature of the Torco process) must depend on an extremely rapid circulation of the hydrogen chloride gas to all the ore particles in the segregation chamber. One wonders, therefore, if a system for the introduction of the sodium chloride into the bottom regions of the chamber might not result in even greater efficiency in the utilization of sodium chloride.

Prof D. D. Howat (Fellow): All of us who have been concerned with the study of chemical reactions at high temperatures are keenly interested in kinetics and are well aware that this is not an easy study experimentally. Dr. Brittan is to be congratulated on the development of neat experimental methods and for his full discussion of the results obtained.

Although the segregation process for the extraction of copper from oxide and silicate ores has been known for almost fifty years, the fundamental chemical and physical changes involved have been little understood and the fundamental data are very scanty. The work now in progress at A.A.R.L., together with that sponsored by the Anglo American Corporation in other research institutions throughout the world, is bound to produce new fundamental data and a much more complete understanding of this rather fascinating process. It is already apparent that some of the old and well-worn chemical reactions that were postulated to occur, just cannot take place in the way which was formerly accepted.

Dr Brittan's work, carefully conducted and thoroughly analyzed as it has been, still leaves us with one great outstanding problem. The thermodynamic data and the possible reactions set out in Table I (page 281) of his paper leave us asking, in complete despair, how can copper be converted into a volatile chloride in the presence of HCl, CO and carbon at temperatures about 800°C?

The thermodynamics all combine to show that copper should be reduced to metal as the first step in the process. This brings us right up against the second problem. If copper were reduced to the metal how would HCl convert it to the volatile chloride?

On top of these problems is the unknown reason for the very high speed of reaction between CO, HCl and the ground copper ore. Still further into the region of the unknown is the reaction by which gaseous hydrochloric acid is produced in the actual process. Perhaps Dr Brittan is feeling grateful that he doesn't have to try to explain this reaction—at this stage of the research programme at least.

The results very clearly show that both CO and HCl gas are essential for rapid production of the volatile copper chloride. Dr Brittan states that 18 minutes were required to attain 83 per cent extraction with HCl gas alone and this was reduced to 4 minutes when CO was

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added to the HCl gas. Fig. 3 of the paper shows how even quite small proportions of CO accelerate the extraction of the copper. Yet there appears to be a maximum volume of CO that can be employed and Fig. 3 indicates that beyond about 4-5 per cent CO there is no significant acceleration in the extraction of copper.

Does Dr Brittain think that this rapid decrease in the effectiveness of the CO with increase in concentration may be due to the production of metallic copper which is then relatively inert to the chloridizing reaction? If this is the case would it not suggest that so far as kinetics are concerned the faster of the two reactions is the reduction of copper oxide by CO?

Obviously the fastest rates of chlorination of the ore are obtained with the appropriate mixture of CO and HCl gas. Does Dr Brittan think that the mechanism of the reaction really involves first the creation of a very highly defective atomic lattice structure on the surfaces of the particles due to the removal of the O atom by the CO followed by the attack on the defective surfaces by the HCl gas? There are numerous instances in which the initial production of a surface layer with a high proportion of atomic lattice defects is an essential for rapid reaction rates subsequently.

Dr Brittain postulates that the reduction of the copper chloride is effected by hydrogen and he suggests that there is a virtually instantaneous reaction

$$Cu_3Cl_3 + \frac{3}{2} H_2 \to 3Cu + 3HCl \quad \ldots \ldots \ldots (6)$$
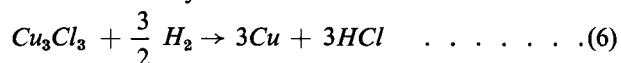
From his thermodynamic data in Table 1, it appears reasonably certain that CO cannot be the reducing agent.

Nevertheless I feel that reaction (6) in relation to the Torco process has to be thought of primarily as involving the nucleation of copper crystals from a gas phase. Possibly the reaction could take place instantaneously if it were possible to accept the precipitation of the copper as a monomolecular layer over a vast precipitation surface. However the essential requirement of the Torco process is that the crystallisation of the copper must be restricted to the developing crystallites on the surfaces of the carbon particles. Otherwise recovery of copper in the subsequent flotation operation would present great difficulties.

Are the kinetics of reaction (6) in relation to the Torco process, not really a study in the kinetics of nucleation of copper crystals. Possibly Dr Brittan is thinking along these lines because he makes reference to unpublished work in which it was shown that when the hydrogen chemisorbed on a carbonacious surface is depleted the reduction of copper chloride ceases. This can probably correctly be interpreted as meaning that hydrogen is the effective reductant for copper chloride. It may, however, also be a pointer to the problem of growing crystals of metallic copper where you want them to grow. This process requires active nucleation sites and the points of chemisorption of hydrogen may in fact provide just such sites. This problem was mentioned in an earlier paper by Mr Pinkney and Mr Plint, who stated that if graphite was used in the process no segregation of copper took place. This, it is accepted can be interpreted as being due essentially to the very low surface reactivity of graphite which just cannot provide the active nucleation sites required.

Author's Reply

Dr Robinson and Professor Howat have raised several interesting points and I wish to thank them for their contributions.

Regarding the first point mentioned by Dr Robinson, we have, in fact, conducted chloridization tests with ore of different mesh size, namely, minus 100 plus 150 mesh and minus 150 plus 200 mesh. With smaller size fractions one experiences difficulties with the fluidization on such a small scale, and even with these somewhat restricted fractions, it was found necessary to vibrate the reactor to preserve good fluidization and thus representative gas-solid contact. The tests were limited to a 2 min reaction time which embraces the rapid initial reaction and where, as a consequence, any effects of diffusion or surface area would be most likely to manifest themselves. The results showed that in the size ranges studied, particle size has no apparent effect on the rate of extraction.

This sort of experiment is, of course, the classic test to determine whether or not intraparticle diffusion is an important rate influencing factor, and the results raise the interesting question as to the mechanism of heterogeneous extraction reactions such as that of the chloridization step of the copper segregation process. The ability of carbon monoxide to accelerate the chloridization reaction would suggest that diffusion within the solid particle is not a rate limiting factor although this

cannot be interpreted unambiguously—as Dr Robinson points out, the carbon monoxide could be responsible for some rupturing of the crystal structure which could assist diffusion or could increase the surface area available for reaction.

However, the lack of influence of particle size on the reaction rate would seem to indicate that it is the resistance of the surface reaction taking place within the particles which is the rate determining step rather than a diffusional mechanism. It would also suggest that the reaction occurs by diffusion of hydrogen chloride into the particles to react with the copper rather than by diffusion of copper ions to the surface. Further indication of this is given by the fact that the partial pressure of hydrogen chloride influences the rate of extraction. The criterion of Weisz and Hicks[9] is normally a useful guide as to whether intraparticle concentration and temperature gradients (and hence diffusion) are factors to be reckoned with, but the necessary diffusivity and thermal conductivity values and the pore size distribution are not easy to come by.

To investigate the point a little further, an attempt was made to characterize the extraction-time data mathematically in terms of the well-known shrinking core solid-fluid reaction model[10] where the diffusional transport is represented by Fick's law. The form of the solution was not commensurate with the rather exponential

character of the experimental extraction data and hence a rate limiting diffusion mechanism would appear to be unlikely. Thus, on the whole, the evidence tends to favour a surface reaction mechanism within the porous structure of the ore particles as being the rate determining factor.

In response to the second point raised by Dr Robinson, the low sodium chloride reagent additions (normally 0.1-0.15 per cent by weight of the ore) during TORCO plant operation do indeed indicate that the loss of chloride from the system is small. In view of the evolution of gas from the top of the bed in the segregation chamber, it would seem that escape of chloride can hardly be avoided. Computation of the flow rate of this gas for a nominal 9 ton/day pilot plant by mathematical modelling techniques (which showed close agreement with the calculated figure of Rey[8] and estimation of the gaseous hydrogen chloride concentration using our latest information, yield a chloride removal figure (even with conservative data) considerably in excess of the chloride added as sodium chloride reagent. This means that re-cycling of chloride to the segregation chamber must occur, a point which warrants further examination. Any hydrogen chloride leaving the top of the bed in the segregation chamber would contact fresh ore entering from the roaster via the connecting slot and also from the cyclones. In addition, if hydrogen chloride managed to enter the roaster, it would encounter the fines leaving the fluidized bed.

As can be seen from the data of the paper, fresh ore reacts very rapidly with hydrogen chloride and thus the contact should effectively capture hydrogen chloride attempting to leave the segregation bed. It is unlikely that the resultant cuprous chloride vapour would be reduced to any extent to regenerate hydrogen chloride even if the roaster were coal fired and unburned carbon remained, since oxidizing conditions prevail in the roaster. Thus, loss of hydrogen chloride in the off-gases should be small. The cuprous chloride, however, would presumably condense in the cooler regions of the cyclones and should thus find its way into the segregation chamber along with the cyclone underflows. It is possible that a little sodium chloride could follow the same route and escape hydrolysis, although this is not very likely in view of the substantial water partial pressures which must exist in the roaster off-gases, and the adequate freeboard temperatures. Confirmatory evidence for return of chloride to the segregation chamber via the cyclone underflows is provided by measurements made at the Rhokana TORCO plant showing chloride concentrations of up to 0.035 per cent in the cyclone dusts.[2]

Concerning the effects of introducing the sodium chloride into the lower regions of the segregation chamber, even if this were the case the gas hydro-dynamics and the hydrogen reduction of cuprous chloride would spread the hydrogen chloride throughout the bed. Consequently, without actually trying such a test (hopefully the technical problems involved in feeding the sodium chloride deep into the bed would not prove insurmountable) it is difficult to foresee whether such a step would result in a decrease in sodium chloride consumption.

With regard to the first point raised by Professor Howat, concerning the thermodynamics of the segrega-tion reactions, one has to draw a distinction between the thermodynamics and the kinetics of the reactions. While the thermodynamics is useful in providing a framework of feasibility for the reactions of interest, it is evident that reaction kinetics holds the key to successful copper

segregation. It is readily apparent, for example, from the extraction-time data presented in the paper that the important chloridization reaction is governed by rate rather than equilibrium considerations. This is no doubt due to the particular mineralization and binding of the copper in the ores studied (which will influence the re-activity of the copper[6]) and, as is pointed out in the paper, these copper minerals cannot be represented by simple compounds as is the case for the thermodynamic data of Table I. Thus, although the thermodynamics would indicate that the equilibrium conversion of copper oxide to copper metal by carbon monoxide reduction is more favourable than its equilibrium chloridization to cuprous chloride with hydrogen chloride, the experimental data in fact show that the *rate* of the chloridization reaction is far greater than that of the reduction reaction. Hence, the copper oxide minerals, in the presence of carbon monoxide and hydrogen chloride in the concentration ranges studied, will tend to chloridize rather than be reduced to metallic form.

The hydrolysis of sodium chloride to produce hydrogen chloride has been extensively studied in our laboratory[4] and while the reaction in the presence of silica was included without amplification in the table of thermo-dynamic data, factors over and above straightforward free energy considerations come into play when relating the reaction to copper segregation. The reaction as written is perhaps somewhat misleading in that solubility between reactants and products exists such that the activity of the condensed phase product is considerably less than unity.[4] This results in far greater hydrogen chloride pressures than would appear to be possible from free energy considerations alone. Furthermore, ore constituents have been observed to exert a profound influence on the reaction. Our own recent experiments have indicated that a mixture of Nchanga Banded Sandstone with 0.5 per cent sodium chloride in the presence of a 20 per cent steam gas phase yielded a hydrogen chloride partial pressure of over 80 mm Hg at 825°C.

The influence of carbon monoxide on the chloridization reaction is certainly an interesting phenomenon. The data of the paper showed that small amounts of carbon monoxide accelerate the chloridization reaction but that above 4.5 per cent and even up to 20 per cent carbon monoxide, no further improvement resulted in the reaction rate. The significant point here is that, while the larger carbon monoxide concentrations did not improve the kinetics, they were not detrimental in that the rate of extraction at 20 per cent carbon monoxide was essentially the same as that at 4.5 per cent. The metallic copper values in the residues remained low even with the higher carbon monoxide concentrations. Thus, even where the carbon monoxide pressure is considerably in excess of the hydrogen chloride pressure, the chloridization reaction is still faster than the *in-situ* reduction to metallic copper.

Any discussion of the mechanism of the chloridization reaction with only macro data at one's disposal must naturally be somewhat speculative. Nevertheless, it provides a complementary sequel to the factors considered above in response to Dr Robinson's query. The behaviour of the carbon monoxide in reaching a saturation con-centration in respect of its ability to accelerate the chloridization reaction is suggestive of a surface reduction reaction within the ore particles prior to chloridization. In other words, once reduction of the surface layer has occurred, further reduction would have to rely on a slow diffusional transport through this layer. However,

with hydrogen chloride present, chloridization will remove the reduced oxide copper thereby exposing fresh surface to carbon monoxide and the cycle can repeat itself. Such a mechanism would be compatible with Professor Howat's observation that numerous systems are known in which the initial production of a surface layer with a high proportion of atomic lattice defects results in accelerated reaction rates.

Regarding the hydrogen reduction of cuprous chloride to produce the segregated copper, little is known about the mechanism of this reaction. Seeing that under TORCO conditions the copper almost invariably deposits on the carbonaceous granules in a form suitable for flotation, of primary concern in a study of the kinetics of segregation was the rate of this reaction rather than its fundamental mechanism. For the overall reduction of gaseous cuprous chloride to form segregated metallic copper, the experimental results confirmed that hydrogen is the effective reductant and demonstrated the reaction to be extremely rapid, these being the significant factors contributing to the viability of the copper segregation process whatever the mechanism by which the copper deposits. What little work there is on copper nucleation has generally been associated with studies of the growth of copper whiskers by halide reduction.[7] But this has not served to resolve whether the deposition occurs by nucleation of copper from the gas phase or as a result of reduction at the surface. It should be noted that copper metal can adsorb substantial amounts of hydrogen at segregation temperatures and since surface diffusion of hydrogen is likely to be extremely rapid at these temperatures, this could account for copper nucleation by reduction at the surface in addition to deposition from the gas phase.

The type of carbonaceous material used will determine the abundance and activity of nucleation sites and thereby will influence the form of the segregated copper. However, in addition to surface activity considerations, the presence of hydrogen at the carbon surface constitutes an important factor determining the effectiveness of a particular carbonaceous sample. Tests in our laboratory have shown that spectrographic graphite containing 0.3 per cent hydrogen yielded moderately good segregation.[5] Furthermore as pointed out in the paper, cuprous chloride was not reduced on a sugar charcoal surface from which the hydrogen had been removed,[3] while graphite in the presence of water resulted in copper deposition from cuprous chloride.[1]

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