Hydrogen Reduction of Copper and Molybdenum Sulphides in the Presence of Lime

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SINCE the conventional pyrometallurgical methods are not acceptable for the extractian of metals from scattered and small deposits of low grade/complex sulphide ores, a number of alternative methods have been considered from time to time for the direct processing of sulphides. Hydrogen reduction of metal sulphides is one such direct reduction technique which has received attention recently primarily because of the possibility of reducing several metal sulphides effectively by hydrogen in the presence of a suitable scavenger for H_2S gas. Thermodynamic considerations show that the incorporation of lime, an inexpensive commercial reagent, in the reduction charge enhance the feasibility of MS-H_2 reactions by three orders of magnitude. As compared with the direct MS-H_2 reactions, the MS-CaO-H_2 reactions (scavenged reduction) possess favourable energetics. Another most attractive feature, arising out of the fact that such a reduction process essentially emits water vapour only, is the possibility of developing new scavenged reduction approaches with negligible atmospheric pollution. Systematic investigations were first conducted to understand the basic parameters influencing the scavenged reduction of pure copper and molybdenum sulphides (Cu_2S and MoS_2) and subsequently the experience so gained was utilized for the treatment of two typical indigenous copper and molybdenum concentrates by the new scavenged reduction approach.

Basic studies on the lime-hydrogen reduction of reagent grade Cu_2S and high-grade MoS_2 powders show that the rate and the extent of reduction of these sulphides are tremendously enhanced by the addition of even theoretical amounts of lime and these results are in accordance with the thermodynamic prediction that scavenged hydrogen reduction of these sulphides must be much more feasible than its direct hydogen reduction. A special feature of the present study has been the detailed investigations conducted on the influence of various experimental parameters on the fixation of sulphur as solid CaS. It was found that the successful practice of scavenged reduction requires use of adequate quantities of lime ($\geq$ a certain CaO/MS mole ratio in each case e.g. 2.0 for Cu_2S and 3.0 MoS_2), moderate temperature of reduction (700-800°C for Cu_2S and 850-900°C for MoS_2), low hydrogen flow rates (0.1-0.2 l/min for both Cu S and MoS) and employment of the sulphide in pellet form and lime as powder. In the case of molybdenum, starting from a 'Climax' MoS_2 concentrate containing 58.8% Mo, it was possible to produce molybdenum powder of over 87% purity which was further consolidated and refined by electron-beam melting to over 99.9% purity.

Experience gained from the basic work on Cu_2S reduction has been made use of for the treatment of a chalcopyrite concentrate from Chitradurga, where the concentrate is produced on a small scale. In this case also the addition of lime to chalcopyrite concentrate was found to profoundly enhance the rate of reduction and drastically decrease the extent of H_2S emission into the off-gas. However, the impact of lime on chalcopyrite reduction was found to be less than that on Cu_2S reduction and this was explained on the basis of the relative thermodynamic stabilities of these sulphides. Pelletizing of the copper concentrate to 2-4 mm size prior to its lime-hydrogen reduction was found to be beneficial. Further, commercial lime was as effective as reagent grade lime as scavenger. For achieving effective mechanical separation of the reduced metallic pellets from the dry slag (CaS-unsued CaO), handling strength of the concentrate/reduced pellets could be improved by the addition of small amounts (<1%) of common binders. Starting from a chalcopyrite concentrate containing 23%Cu,

it was possible to desulphurise the concentrate to over 97% level and prepare reduced pellets analysing 38% Cu which were subsequently upgraded to 77% Cu by a selective HCl leaching procedure (for Cu-Fe separation). A conceptual flowsheet has been suggested for copper extraction by this scavenged reduction approach.

Jaduguda molybdenite concentrate is obtained as a byproduct of uranium mining in this country and as yet no flowsheet has been developed for its treatment. The said concentrate is of low grade (41% Mo) and a pretreatment procedure was devised in the present work for its upgrading It consisted of soaking this MoS_2 concentrate in rectified spirit followed by its leaching with an acid mix, respectively, for improving its wettability by the acid solvent and for removal of its gangue. The upgraded concentrate (57% Mo) was then successfully reduced by hydrogen in the presence of lime utilizing the conditions established earlier. The reduced product (96-97% Mo), which was separated from the dry slag mechanically or by acid leaching, was compacted, arc-melted and the electron-beam melted under high vacuum to prepare lustrous molybdenum buttons of over 99.9% purity. Results of these studies have been utilized to suggest a conceptual flowsheet for molybdenum extraction from its low grade concentrates.

Although the present investigations were primarily concerned with applied work on the lime-hydrogen reduction of two sulphides and their concentrates, it was felt interesting to examine the probable reaction path and the morphological features in the Cu_2S-CaO-H_2 reaction. The reaction is considered to proceed by two successive gas-solid reactions *viz.* Cu_2S-H_2 and CaO-H_2S and of these, the latter was ruled out on the basis of relevant thermodynamic calculation and experimental results. Morphological aspects of the reduction of Cu_2S pellets were also observed by SEM studies carried out as a function of temperature and time. Reduction at morderate temperatures was found to result in the formation of copper fibers, associated with a moderate activation energy value which is in close agreement with that for self-diffusion of copper in copper. High temperature reduction resulted in the formation of sintered crusts of copper, associated with a low activation energy value characteristic of mass-transport through stagnant gas boundary layer.

The present study contributes to a proper appreciation of the role of lime in developing new reduction approaches with minimal pollution and identification of the factors critically influencing scavenged reduction practices. Further it also demonstrates the possibility of developing new scavenged reduction approaches for the extraction of copper and molybdenum by the direct hydrogen reduction of their concentrates.

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