EXTRACTION OF METALS FROM MULTIMETAL SULPHIDE CONCENTRATES THROUGH CHLORIDE ROUTES

by

P.K. Jena[1] and E.A. Brocchi[2]

Due to increasing demand of Cu, Ni, Pb, and Zn, their individual sulphidic ores are fast depleting and hence all over the world, efforts are being made to mine, beneficiate and extract these metal values from various grades of complex ores. Due to difficulties in producing individual concentrates, generally the bulk concentrates are prepared and processed for developing methods to extract the metals. In this paper, four different chloride processes namely ferric chloride leaching, slurry chlorination, dry chlorination and ammonium chloride roasting followed by leaching with water, have been examined for treating the multimetal sulphide concentrates. Some of the salient features of the results obtained by applying these processes to three different sulphide concentrates, have been highlighted. Based on these findings, the research and developmental programmes undertaken by the authors on a bulk sulphides concentrate from Brazil, have been outlined.

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1. Visiting Professor, DCMM-PUC, Rio de Janeiro, Brazil and President, NRDF, Lewis Road, Bhubaneswar, 751002, India .

2. Associate Professor, DCMM-PUC, Rio de Janeiro, Brazil.

1. INTRODUCTION

Due to increasing production of nonferrous metals like Cu, Ni, Pb and Zn and fast depletion of their individual ores, in recent years, special attention is being paid to process their multimetal sulphide ores and concentrates. Further, due to complex nature of these ores, it is difficult to produce individual concentrates of the metals without sacrificing the yield and quality. Therefore, efforts are being made all over the world to process their bulk concentrates to obtain the individual metals. Flotation technique is generally used to beneficiate the multimetal sulphide ores.

Elkem[1] and CANMET[2] have investigated ferric çhloride leaching in small but continuous reactors, for treating bulk concentrates of Cu, Pb, Zn and Ag. In these cases, the dissolution of metal values is effected by ferric chloride alone or its combination with cupric chloride solution. Dutrizac and MacDonald[3] have reviewed the earlier studies on dissolution of sulphide minerals in ferric ion solutions. Jena and coworkers[4,5,6] have made detailed studies on the kinetics of dissolution of the individual sulphide minerals of Cu, Pb and Zn and their bulk concentrates in ferric chloride solution. Recently, studies have been carried out by the authors[7] on slurry and dry chlorination of a Brazilian chalcopyrite concentrate for establishing experimental parameters for extraction of copper as well as suggesting the mechanism of both the processes involved. Recently Jena and Coworkers[8] have developed a process for nearly complete extraction of Cu and Ni from a complex sulphide concentrate of China by ammonium chloride roasting at a temperature lower than 400°C followed by leaching with water at room temperature.

In this paper, a brief discussion on the Chemistry of the above mentioned processes, has been made. Some of the salient results on the application of these processes to three types of sulphide concentrates, have been incorporated. The R&D Programmes undertaken by them on a Brazilian Complex Sulphides concentrate of Cu, Pb and Zn, have been outlined.

2. CHEMISTRY OF THE PROCESSES:

Four possible processes namely, (a) ferric chloride leaching, (b) slurry chlorination by chlorine, (c) dry chlorination by chlorine and (d) ammonium chloride roasting followed by water leaching, for treating Cu-Pb-Zn Sulphide concentrates, have been considered.

2.1 The stoichiometries of the individual reactions for the dissolution of galena, sphalerite and chalcopyrite in ferric chloride solution, have been reported[4] to be.

$PbS + 2FeCl_3 = PbCl_2 + 2FeCl_2 + S^\circ$ .... (1)

$ZnS + 2FeCl_3 = ZnCl_2 + 2FeCl_2 + S^\circ$ .... (2)

$CuFeS_2 + 4FeCl_3 = CuCl_2 + 5FeCl_2 + 2S^\circ$ ...... (3)

Each of these reactions were found to follow the simple shrinking core model, following the rate equation, $1-(1-R)^{1/3} = kt$ .... (4) where 'R' is the fraction of the mineral reacted in time 't' and 'k' is the rate constant. The reaction order values with respect to ferric chloride concentration were found to be 0.76, 0.62 and 0.38 for galena, sphalerite and chalcopyrite respectively and the respective activation energy values were found to be 50, 58 and 93 KJ/mole.

These kinetic values have been predicted and applied successfully to the ferric chloride dissolution of bulk sulphide concentrates of Cu, Pb and Zn[5].

2.2 Dry chlorination of the sulphides of Cu, Pb and Zn are suggested to be taking place as per the following overall reactions.

$PbS + Cl_2 = PbCl_2 + S^\circ$ .... (5)

$ZnS + Cl_2 = ZnCl_2 + S^\circ$ .... (6)

$CuFeS_2 + 2.5Cl_2 = CuCl_2 + FeCl_3 + 2S^\circ$ .... (7)

The authors have recently carried out studies on kinetics of dry chlorination of a Brazilian Chalcopyrite Concentrate[7]. The effect of partial pressure of chlorine (PCl_2) at 400°C has been studied and the extent of chlorination of copper sulphide has been found to be independent of PCl_2 beyond 0.4 atm. The decomposition of the intermediate complex, $CuS-Cl_2$ formed by the Chemisorption of Cl_2 on CuS surface, has been suggested to be the rate determining step as per the following reaction:

$CuS(s) + Cl_2(g) \quad CuS-Cl_2 \quad slow \quad CuCl_2 + S^\circ$. (8)

The activation energy of the process has been found to be 6.1 Kcal/mole in the chlorination temperature range of 350° to 450°C. Nearly complete chlorination of copper present in the chalcopyrite concentrate (97.5%), has been possible at 400°C by chlorination for 20 minutes with a PCl_2 value of 0.6 atm. in nitrogen.

2.3 Water slurry chlorination of the chalcopyrite concentrate, has also been carried out by the authors[7] by chlorine gas at room temperature, using various solid-liquid ratios (5 to 20% by wt. of the concentrate in water).

The amount of copper chlorinated has been found to be proportinal to the square root of the partial pressure of chlorine (PCl_2 0.5). The rate of reaction was found to fit with the topochemical reaction model as suggested in equation (4). From these results, the slurry chlorination have been suggested to take place in the following manner.

$Cl_2(g)$ fast $2Cl$ (aq) .... (9)

$CuS + Cl(aq)$ slow $CuSCl$ .... (10)

$CuSCl + Cl(aq)$ fast $CuCl_2 + S°$ .... (11)

The slurry chlorination has been found to decrease with increase in temperature (as solubility of chlorine gas in water decreases with increase in temperature); this further confirms the suggestion made earlier that chlorine gas first goes in to solution in water before reacting with CuS. The amount of chlorination of the metal value per unit time, has been found to decrease with increase in percent of the concentrates in the slurry. This supports the suggestion that the surface reaction as given in equation (10), may be rate controlling.

2.4 Another method for opening up a multimetal sulphide ore or its concentrate, is to treat it with ammonium chloride at a moderate temperature and then leach the chloridised product in water at room temperature. In such a case, the metals like Cu, Ni and Zn would form their respective chlorides and ammonia possibly forms its sulphide. The reaction of ammonium chloride roasting of a sulphide can be expressed by the general chemical equation:

$MeS + 2NH_4Cl = MeCl_2 + (NH_4)_2S$ .... (12)

Where Me stands for Cu, Ni, Zn, etc.

It is very likely that ammonium chloride in solid or gaseous or in both forms, depending on the temperature of reaction, reacts with the metal sulphides. At higher temperatures of chloridise roasting, some of the ammonium sulphide is likely to decompose to ammonia and hydrogen sulphide.

3. TREATMENT OF SOME SULPHIDE CONCENTRATES:

The processes applied to extract the metal values from three different sulphide concentrates are (1) ferric choride leaching (2) slurry and dry chlorination with chlorine and (3) low temperature ammonium chloride roasting followed by leaching with water. For ferric chloride leaching, a complex sulphides concentrate of India, for slurry and dry chlorination with Cl_2, a chalcopyrite concentrate from Brazil and a Chinese multimetal sulphides concentrate for ammonium chloride roasting, have been used. The analyses of these three are given in Table 1.

TABLE 1

Analyses of different sulphides concentrates used

Nature and Locations of the Sulphides	Analysis (%) of major constituents					
	Cu	Ni	Zn	Pb	Fe	S
Bulk Cu-Pb-Zn Complex Sulphides Concentrate of India (Gujrat)	3.60	-	20.20	12.60	13.00	26.20
Chalcopyrite Concentrates of Brazil (Salobo)	34.46	-	-	-	16.60	11.90
Concentrate of Cu-Ni-Fe Sulphides of China (Jinchuan Mine)	5.22	6.90	-	-	29.43	14.75
Brazilian Cu-Pb-Zn Complex Sulphides Concentrate (Palmeiropolis)	6.30	-	16.00	3.80	25.50	30.90

3.1 As mentioned earlier, the kinetics of the individual sulphide concentrates of Cu, Pb and Zn in ferric chloride solution have been studied[4]. Utilizing these results, the extent of dissolution of the metals, present in their complex sulphides concentrate in aqueous solution of ferric chloride, has been calculated for different experimental conditions and found to agree reasonably well with the experimental values. Some of these results are given in Table II. By proper selection of the temperature, time and ferric chloride concentration, it has been possible to predict from the kinetics data the degree and selectivity of metal extraction (approximately) from the complex sulphide concentrates.[5] For example, it has been calculated that 100% each of Pb and Zn with only 1.7% Cu can be selectively leached out in 0.3M $FeCl_3$ solution at 70°C in 2 hours, where as actually it has been possible to extract 90.2% Pb, 91.2% Zn and 5.0% Cu. By leaching the same ore by 4M $FeCl_3$ solution at 100°C for 5 hours, 91.5% Pb, 93.45 Zn and 84.5% Cu could be extracted where as the calculated values are 100% in each case.

TABLE 2

Comparision of metal values calculated and found experimentally (given in parentheses) in ferric chloride leaching of Cu-Pb-Zn sulphides concentrates of India.

$FeCl_3$ Conc. (M)	Temp(°C)	Time (min.)	% Metal extracted		
			Pb	Zn	Cu
0.3	70	15	100 (92.7)	19.8 (19.1)	0.2 (nil)
0.2	60	60	100 (92.4)	32.4 (33.1)	0.25 (7.5)
0.2	60	120	100 (98.2)	64:9 (58.2)	0.5 (4.6)
0.2	100	10	100 (93.3)	52 (46.5)	1.6 (12)
0.3	60	120	100 (92.3)	87.3 (84.1)	0.6 (5.0)
0.3	70	120	100 (90.2)	100 (91.2)	1.7 (5.0)
0.2	100	180	100 (98.9)	100 (97.7)	28.8 (33.0)
4.0	100	300	100 (94.5)	100 (93.4)	100 (84.4)

3.2 The dry chlorination of chalcopyrite concentrate of Brazil by chlorine gas has been carried out in the temperature range of 350°C to 450°C[7]. By using a chlorine gas flow rate of 250ml per minute, it has been possible to extract copper completely at 400°C at a partial pressure of Cl_2 of 0.8 atm in 20 minutes.

The same grade of concentrate has also been used for chlorination in an aqueous slurry. With 5wt% of the concentrate in the slurry, 100% Cu has been chlorinated at 30°C in only 5 minutes by passing 200ml Cl_2 per minute. With increase in solid-liquid ratio, the extent of chlorination of Cu has been found to decrease for a certain period. For example, at 30°C, by using a Cl_2 flow rate of 200ml per minute for 30 minutes, it has been possible to extract 100,87 and 68% of copper in the slurries containing 10,15 and 20% of the concentrates respectively. In Fig. 1, a comparison of slurry chlorination at 30°C with that by dry chlorination at 400°C has been made. At 17 minutes, both the chlorination values are found to be nearly same (about 88%). However, slurry chlorination is preferred because of room temperature operation.

3.3 Studies have been carried out by Jena et al[8] to extract Cu and Ni from a Cu-Ni-Fe sulphide concentrate of China, by chloridisation with ammonium chloride in a temperature range of 300°C to 450°C followed by leaching with water at room temperature. By treating the concentrate with 25 percent (by wt. of the conc.) of ammonium chloride at 400°C for 10h, it has been possible to extract 99% Cu, 94% Ni with 16% Fe. Similar studies have also been carried out by Jena and Coworkers[9] on bulk concentrates of Indian Complex Sulphide ores of Cu, Pb and Zn with good recovery of the metal values.

4. STUDIES ON BRAZILIAN Cu-Pb-Zn SULPHIDES CONCENTRATE

Brazil has a sizable deposit of the mixed sulphides of copper, lead and zinc. The bulk concentrates from these ores have been prepared by flotation[10] and supplied for these studies. The analysis of the bulk concentrate is given in Table 1 The following studies on extraction of Cu, Pb and Zn from the concentrates through chloridisation routes, have been undertaken.

(a) After examining the selective chlorination of Cu, Pb and Zn sulphides present in the concentrate by both dry and slurry chlorination separetely, different steps in both the processes are to be suitably applied to develop a flow diagram,

(b) The slurry chlorination by Cl_2 followed by $FeCl_3$ leaching as suggested for the Indian complex sulphide ore[8] are being tried for the Brazilian concentrate.

(c) As Cu-Ni-Fe Sulphides concentrate as well as bulk concentrates of Cu-Pb-Zn Sulphides have resulted in better metal extraction, through low temperature ammonium chloride roasting followed by leaching with water, it has been felt worth while to apply this process also to the Brazilian multimetal sulphides concentrates.

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