

RECOVERY OF METAL VALUES FROM COPPER CONVERTER AND SMELTER SLAGS BY FERRIC CHLORIDE LEACHING

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ABSTRACT

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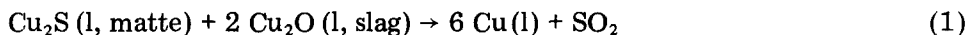
A study of the recovery of copper, nickel and cobalt from copper converter and smelter slags by leaching with ferric chloride is reported. The converter slag from Ghatsila, India contained 4.03% copper, 1.99% nickel and 0.48% cobalt and the smelter slag contained 1.76% copper, 0.23% nickel and 0.19% cobalt. Various parameters including the effect of stirring, leaching time, leaching temperature, concentration of ferric chloride, solid-liquid ratio and particle size, on the extraction of copper, nickel and cobalt have been studied. 92% copper, 28% nickel and 24% cobalt could be extracted from converter slag under optimum conditions, whereas 54% copper, 71% nickel and 44% cobalt could be extracted from smelter slag.

INTRODUCTION

Large quantities of smelter slag and converter slag are produced by copper smelters at Ghatsila (Bihar) and Khetri (Rajasthan), India. The entire quantity of smelter slag which contains considerable amounts of copper, nickel and cobalt is dumped every year. Though it is a common practice to add converter slag to the smelter charge to recover most of the copper and nickel, at no stage is cobalt recovered. Moreover the addition of converter slag to the smelter charge makes the charge to metal ratio unnecessarily high. A recent study (Kupryakov and co-workers, 1974) shows that addition of converter slag to a reverberatory furnace charge increases the slag volume and copper loss. Moreover Mashur'yan and co-workers (1974) while examining the causes of copper, nickel and cobalt losses in the slag from reverberatory furnace smelting found that halting the addition of converter slag to the furnace decreased the thickness of the magnetite incrustation on the furnace bottom, increased the smelting rate by 10–15% and also decreased the non-ferrous metal loss, especially that of cobalt, in the slag. Thus it was thought worthwhile to find an alternative route for the recovery of metal values from converter and smelter slags.

In waste copper smelting slags the bulk of the copper is present as small

droplets of copper metal, coated with copper-iron sulphides, about 50 μm in diameter (Shelley and Shelley, 1974). The proportion of copper in smelter slags occurring as metal-matte prills ranges from 70–96% (Shelley and Shelley, 1974). The main slag matrix consists of fayalite, pyroxenes, mellilite and glass. The chief metallic mineral in the sample is magnetite, while the copper value is present as chalcocite with minor occurrences of bornite, chalcopyrite, covelite, copper oxide and metallic copper (Chakrabarthy, 1977). The copper in converter slags is in the form of: (i) copper oxide dissolved in the slag due to highly oxidising conditions in the converter; (ii) entrained matte (sulphide) and (iii) metal from the reaction: (Biswas, 1976)

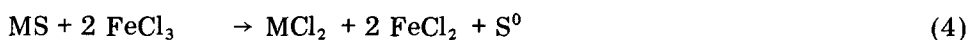
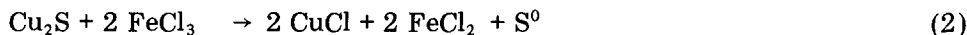


Nickel and cobalt are also present as a mixture of sulphide, oxide and metal in varying proportions.

Hydrometallurgical techniques have been used to recover copper both from its sulphides and oxides. Methods of recovering copper from sulphide minerals include: sulphating roast followed by a water/acid leach (Griffith et al., 1975); oxidative ammonia leaching (Evans et al., 1964); oxidative aqueous leaching (O'Connor, 1952); ferric sulphate leaching (Dutrizac et al., 1969, 1970) and ferric chloride leaching (Haver and Wong, 1971; Haver, Baker and Wong, 1975). The extraction of metal values from copper smelter and converter slags through hydrometallurgy remains somewhat unexplored. Leaching only of copper values from copper smelter slag with acidic ferric sulphate solutions and with ammonia-ammonium carbonate solutions at atmospheric pressure has been reported recently (Shelley, 1975). About 50% extraction of copper was achieved from a slag containing about 0.55% copper when around sixteen times the stoichiometric amount of ferric iron was used for leaching. Using dilute ammonia-ammonium carbonate solutions containing 1.9% ammonia and 1.3% carbon dioxide for leaching, an extraction about 70% of the copper was reported after grinding the slag to 95% less than 63 μm .

As ferric chloride can oxidise metallic copper, nickel and cobalt as well as their sulphides, this paper reports studies on the leaching of copper converter and flash smelter slags with ferric chloride with a view to exploring the possibility of extracting all three metals from them.

Ferric chloride solution will dissolve sulphides and to some extent oxides of copper, nickel and cobalt (or their metals if present) to give cuprous chloride, nickel chloride and cobaltous chloride, respectively.



where M stands for Ni or Co. Thus the extent of extraction of copper, nickel

and cobalt may still depend on the proportion of each metal present in the slags as sulphide, oxide or free metal.

EXPERIMENTAL

The copper converter and flash smelter slags were obtained from the Indian Copper Complex, Ghatsila, India. All the reagents employed were of analytical reagent grade. The slag samples were first crushed in a jaw crusher, then in a roll crusher and finally ground in a ball mill. Copper was estimated by the iodometric method; nickel gravimetrically as the Ni-dimethylglyoxime complex and cobalt colorimetrically using nitroso-R-salt as reagent (Vogel, 1962). The interference due to copper in the estimation of nickel and cobalt was removed by extracting the copper completely and selectively at pH = 2 with 25% LiX 64N in kerosine. Calcium and magnesium were estimated volumetrically by the EDTA method; silica and alumina were estimated gravimetrically (Vogel, 1962). Typical chemical analyses of the copper converter and smelter slags used in these investigations are given in Table 1.

TABLE 1

Chemical analysis of slags

Constituent	Amount (%)	
	Converter slag	Smelter slag
Copper	4.03	1.76
Nickel	1.97	0.23
Cobalt	0.49	0.19
Iron	38.32	46.46
Calcium	4.01	2.09
Magnesium	2.66	0.97
Silica	34.32	33.57
Alumina	0.08	1.58

Leaching studies

Studies on the leaching of the slags with ferric chloride solution were carried out in a 500 ml three necked glass vessel fitted with a mechanical stirrer, condenser and thermometer. Heat was supplied using a heating mantle fitted with an energy regulator. A weighed amount of the ground slag was placed in the flask and a suitable amount of ferric chloride solution added. The reaction was allowed to continue at a definite temperature for the required period of time. The temperature of the reaction mixture was controlled to about $\pm 1^\circ\text{C}$. After the reaction was over the slurry was filtered, washed and the filtrate was made up to a definite volume. The amounts of ferrous iron,

ferric iron, copper, nickel and cobalt in the leach solution were then determined.

RESULTS AND DISCUSSION

Various parameters including the effect of stirring, solid-liquid ratio, leaching time, temperature, particle size and the amount of ferric chloride on the extraction of metal values from the slags were studied to determine the optimum conditions.

Converter slag

Table 2 shows the effect of stirring on the extraction of metal values from converter slag. Without stirring the extraction was quite low but with a stirring speed of 100 rpm copper extraction was increased by almost 18% whereas nickel and cobalt recoveries showed 4 to 5% increase. Further increasing the rate of stirring gave no significant improvement in extraction.

TABLE 2

Effect of stirring rate on Cu, Ni and Co extraction

Temperature 85°C, time 2½ h, particle size 150 µm, ferric chloride stoichiometric.

Stirring rate (rpm)	Metal extracted		
	Cu	Ni	Co
Nil	55.0	14.5	9.0
100	83.1	17.4	16.1
200	83.1	18.7	16.7
300	83.1	19.0	17.2

The solid-liquid ratio was varied between 10 and 40% solids. The recovery of metal values was not dependent on the dilution of the leach solution. At all solid-liquid ratios, the extraction of copper, nickel and cobalt under similar conditions as in Table 2, were 84, 20 and 18%, respectively. From these results it is evident that ferric ion concentration had no effect on the extraction of metal values in the range studied.

It can be seen from Fig. 1 that a leaching time as short as 15 min resulted in about 79% copper extraction though nickel and cobalt recoveries were limited to 8 and 11%, respectively. The extraction of the metals showed a gradual upward trend as leaching time increased from 15 min to 2 h after which the percentage extraction of copper and cobalt remained practically constant, although there was a marginal increase in nickel extraction.

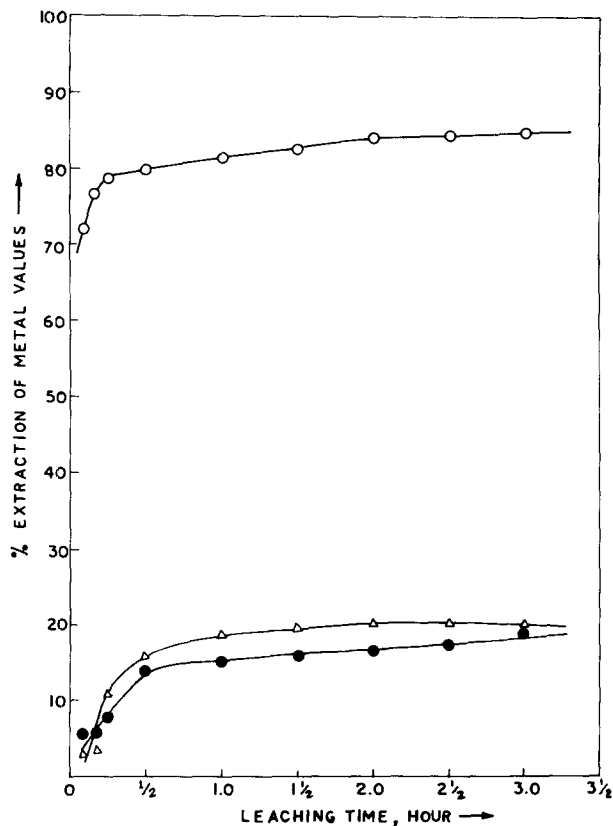


Fig. 1. Effect of time on extraction of metal values from converter slag. Temperature 85°C; ferric chloride stoichiometric; S/L ratio 1:10; particle size < 150 μm ; stirring speed 200 rpm; 10 g of slag; \circ , copper; \bullet , nickel; Δ , cobalt.

Figure 2 shows the effect of temperature on the recovery of metal values. The dissolution of copper was rapid even at ambient temperature, as about 64% copper is recovered at 29°C, whereas at this temperature the extraction of nickel and cobalt were 6.5% and 1.5% respectively. By increasing the temperature, the extraction of copper and nickel increased gradually to 90 and 23.5%, respectively, at 100°C. In the case of cobalt there was no appreciable increase in extraction until the temperature was increased to 55°C and thereafter it increased to about 23% at 100°C. Using the above data, approximate energies of activation for the extraction of copper, nickel and cobalt were calculated using the Arrhenius equation and were found to be 2.5, 3.4 and 2.7 kcal mole⁻¹ (10.5, 14.2 and 11.3 J mole⁻¹).

From Fig. 3 it can be seen that the extraction of copper increased slowly with decreasing particle size of the slag from 420 μm to 350 μm and thereafter increased steeply as the particle size decreased from 350 μm to 105 μm , beyond which the extraction remained more or less constant at 83%. A some-

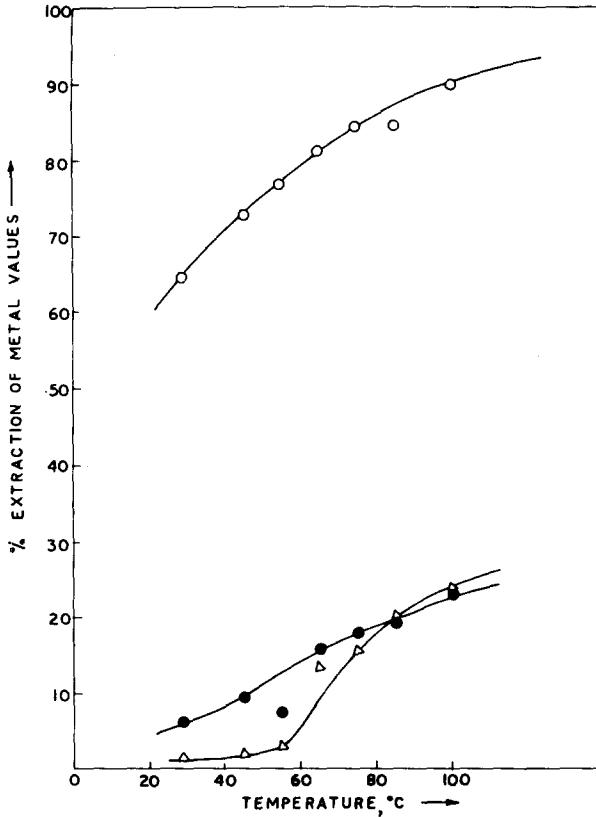


Fig. 2. Effect of temperature on extraction of metal values from converter slag. Time 2½ h; ferric chloride stoichiometric; S/L ratio 1:10; particle size < 150 μm ; stirring speed 200 rpm; 10 g of slag; \circ , copper; \bullet , nickel; \triangle , cobalt.

what similar behaviour was observed in the case of cobalt, although a gradual increase in the extraction of nickel was observed throughout the range of particle size studied. The sudden jump in the extraction of copper from 38% at between 420 and 300 μm to 57 and 83% with the particle size ranging from less than 300 μm to 150 μm and between 150 and 105 μm respectively may be due to the liberation of copper at these size fractions resulting in better contact between ferric chloride and the reactant. Shelley (1975) also observed that an optimum particle size of 125 μm to 200 μm was required to sufficiently expose the copper present in the slag.

Figure 4 shows the dependence of the recovery of metal values on the ferric ion content of the solutions. 1.53 g ferric iron/100 ml of solution used for leaching 10 g slag was about the minimum required to achieve 92% copper recovery, though nickel and cobalt recoveries were 23.0 and 24.0% respectively. This amount of ferric iron appeared to be the optimum as a further increase did not substantially increase the extraction of nickel and cobalt.

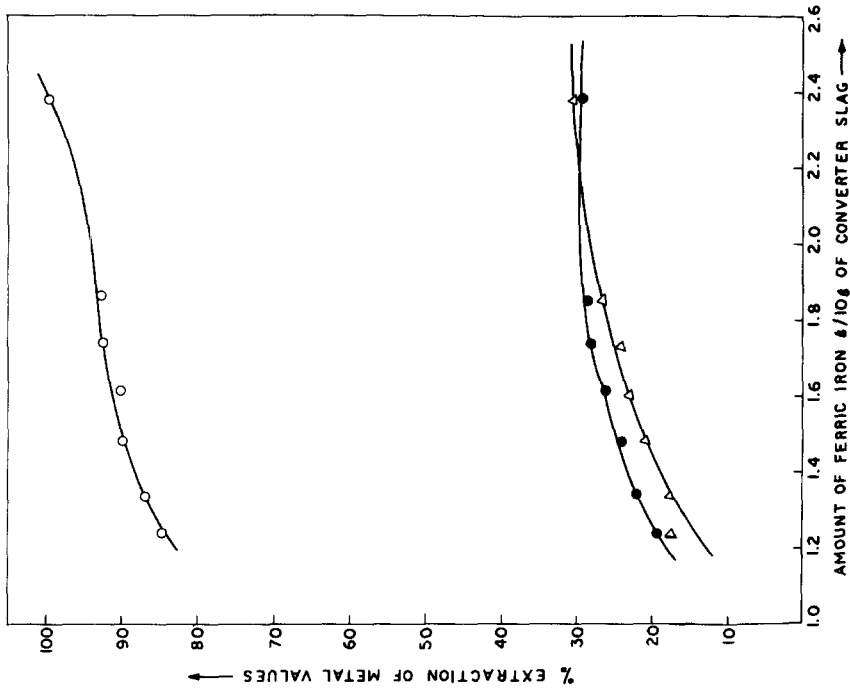


Fig. 3. Effect of particle size on extraction of metal values from converter slag. Time 2½ h; temperature 85°C; ferric chloride stoichiometric; S/L ratio 1:10; stirring speed 200 rpm; 10 g of slag; ○, copper; ●, nickel; △, cobalt.

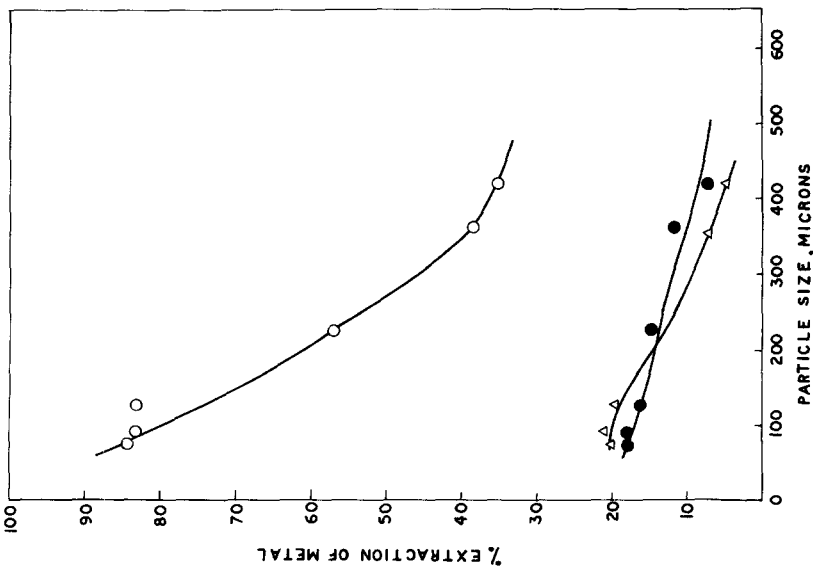


Fig. 4. Effect of the total iron on the extraction of metal values from converter slag. Time 2½ h; temperature 85°C; particle size < 150 μm; stirring speed 200 rpm; S/L ratio 1:10; 10 g of slag; ○, copper; ●, nickel; △, cobalt.

Smelter slag

At the optimum conditions obtained for recovering the metal values from converter slag (as discussed above), the percentage extractions obtained with smelter slag were: copper nil, nickel 8% and cobalt 2.5%. To improve the extraction, the ferric ion content of the leach solution was increased gradually (Fig. 5). It is clear from Fig. 5 that by using 4.1 g of iron/20 g of smelter slag, which is equivalent to five times the stoichiometric amount, copper extraction was increased to 54%. These results confirm Shelley's (1975) observation that a large excess of ferric iron was needed to achieve about 50% extraction from smelter slag.

Figure 6 shows the effect of particle size on percentage recovery of copper, nickel and cobalt. Copper recovery is maximum between 150 and 105 μm (Shelley, 1975) whereas for nickel and cobalt the optimum sizes are below 53 and between 75 and 53 μm , giving 71.0 and 44.0% extraction, respectively. Due to the less oxidising conditions prevailing in the smelting step, it appears that nickel and cobalt in the smelter slag are present as sulphide to a larger extent than in converter slag and hence get liberated more easily at finer size fractions.

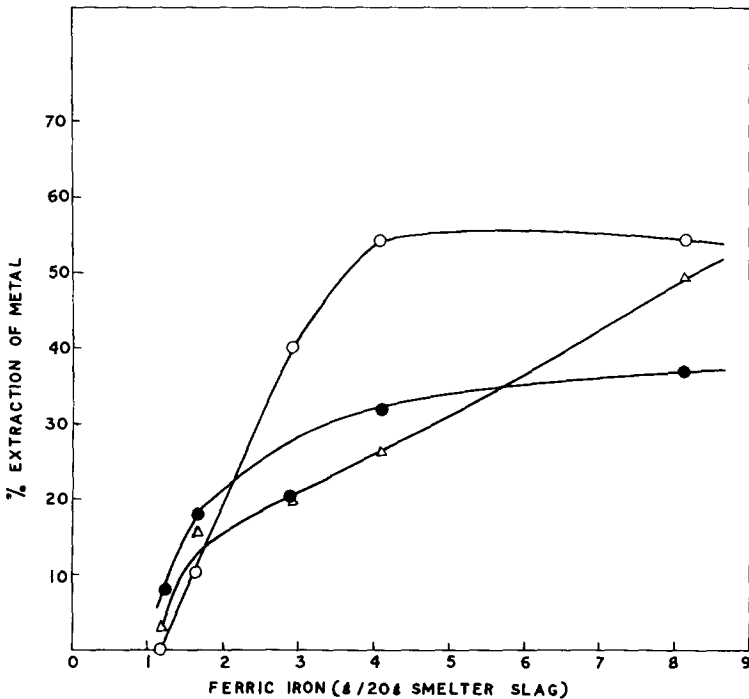


Fig. 5. Effect of the total iron on extraction of metal values from smelter slag. Time 3 h; temperature 100°C; S/L ratio 1:10; particle size < 150 μm ; stirring speed 200 rpm; 20 g of slag; \circ , copper; \bullet , nickel; \triangle , cobalt.

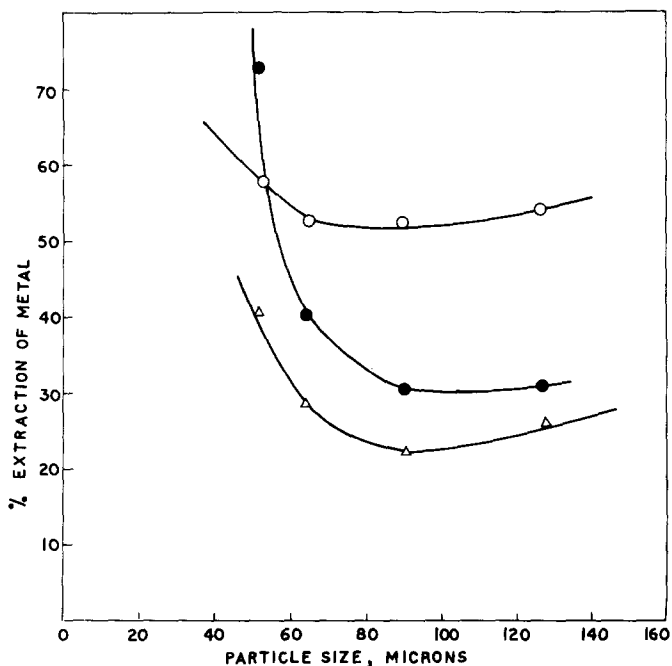


Fig. 6. Effect of particle size on extraction of metal values from smelter slag. Temperature 100°C; time 3 h; ferric chloride 5 times stoichiometric; stirring speed 200 rpm; S/L ratio 1:10; 20 g of slag; ○, copper; ●, nickel; △, cobalt.

Figure 7 shows the effect of time on the extraction of the metals from smelter slags. The extraction of copper remained steady beyond 3 h leaching time; the extractions of nickel and cobalt increased to 34.0 and 44.0% from 26.0 and 31.0% respectively by increasing the leaching time from 3 to 6 h. Further increase in the leaching time to 12 h did not improve the extraction of the metals.

Analysis of the leach liquors for ferric and ferrous iron showed that more ferrous iron was formed than could be accounted for by the consumption of ferric iron in the extraction of copper, nickel and cobalt. This excess formation of ferrous iron was found to be partly due to the metallic iron or iron sulphide present in slags and partly due to the dissolution of iron oxides in the free acid present in ferric chloride solution. This explains why more ferric chloride than the stoichiometric requirement was needed for the extraction of metal values, especially in the case of dump slag where the percentage of iron was very high and the percentage of metal values quite low.

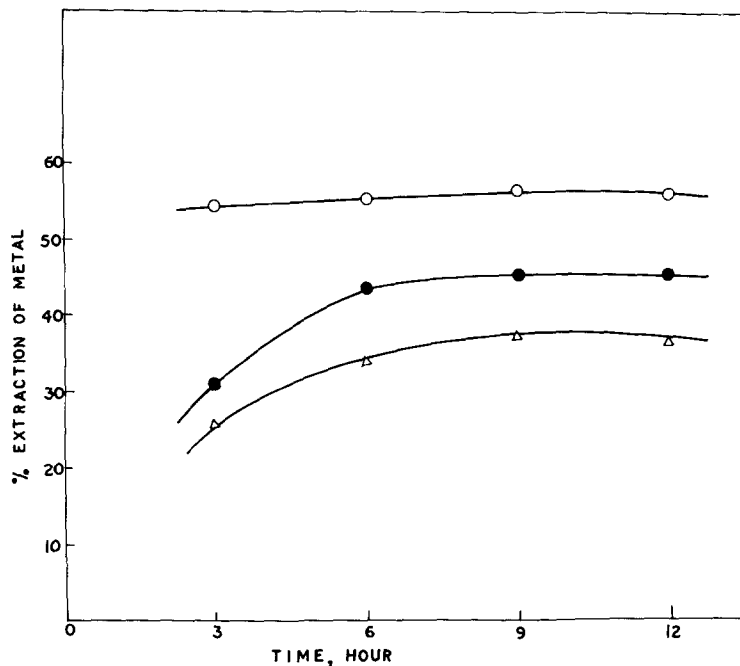


Fig. 7. Effect of time on extraction of metal values from smelter slag. Temperature 100°C; ferric chloride 5 times stoichiometric; particle size < 150 μm ; stirring speed 200 rpm; 20 g of slag; \circ , copper; \bullet , nickel; Δ , cobalt.

CONCLUSION

Ferric chloride leaching seems to be quite effective for the extraction of copper completely from converter slag. However, for smelter slag it was difficult to extract copper beyond 54%. The difference in the extraction capacity is probably due to the different proportions of sulphide, oxide and metallic copper and iron present in the two slags. With decreasing particle size beyond 150 μm , nickel and cobalt extraction from converter slag did not increase, though the extraction of nickel and cobalt from smelter slag was markedly improved to 71.0 and 44.0%, respectively, at a particle size of 53 μm . The optimum experimental conditions for converter slag leaching were: particle size less than 150 μm , time 2½ h, temperature 85°C, amount of ferric chloride 1.25 times stoichiometric, giving extractions of copper 92.0%, nickel 28.0% and cobalt 24.0%. For smelter slag the optimum conditions were: particle size less than 53 μm , leaching time 6 h, temperature 100°C, amount of ferric chloride five times stoichiometric with extractions of copper 54.0%, nickel 77.0% and cobalt 44.0%.

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