Utilization of ferro-manganese slag for production of manganese sulphate and Electrolytic manganese metal/manganese di-oxide

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ABSTRACT

High and low ferro-manganese slags have been studied for production of manganese sulphate which forms the intermediate product for production of electrolytic manganese metal/ di-oxide. With low manganese slag, a recovery of 72% manganese is obtained with 100% excess acid in the spent liquor over the stoichiometric equivalent to contained manganese in the slag with the granulated slag ground to -100 mesh. This recovery increases to 80% when the slag is ground to -200 mesh. With high manganese slag, a recovery of 86% is obtained with 37% excess acid. This recovery increases to 95% with excess acid, but aluminium and silicon going into the leached solution increases more than doublefold. The leached purified manganese sulphate solution is found quite suitable for production of EMM/EMD/CMD.

Introduction

Indian manganese ores mostly contain higher oxides of manganese and as such, are not soluble appreciably in the cell effluent from electrolytic manganese metal or dioxide cells containing 30-50 gm per litre of sulphuric acid. Hence in the usual process for production of electrolytic manganese metal/dioxide the higher oxides of manganese in the ore has to be converted to the acid soluble lower oxides of manganese as a first step. This is usually carried out by giving a reduction roast at about 600°C to the manganese ore with one of the industrial reductants, such as, fuel oil, charcoal, coke or coke oven gas. On the other hand, manganese in the slag is present as manganese silicate (MnO, SiQ₂ and 2 MnO, SiO₂) which is decomposed and dissolved in the sulphuric acid present in the cell effluent. An advantage of using ferro-manganese is that it needs no pre-reduction as in the case with manganese ores. This reduction step in the usual process as practised with manganese ores, can be eliminated while using the manganese slag for production of electrolytic manganese.

However, there is a major disadvantage in using slag since it usually contains other constituents which would consume sulphuric acid. For example, calcium and barium present in the

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slag would react with sulphuric acid available in the spent liquor and precipitate out as calcium and barium sulphate in the leaching tank. The sulphuric acid consumed by these elements are hence lost from the electrolyte circuit.

Aluminium, magnesium and potassium also enter into the leached solution. During the purification stage for removal of iron, aluminium is precipitated out. However, the precipitated aluminium hydroxide together with the silicic acid in solution forms a gel which would cause filtration difficulties. Magnesium upto 8 g/L has no deleterious effect on the operation of the manganese metal cell. Beyond this limit, crystals of manganese - magnesium - ammonium sulphate forms, especially when the temperature falls below 25°C. Similarly, potassium above 0.05 g/L in solution is deleterious in the production of EMD.

On the whole, the economic production of electrolytic manganese metal/manganese dioxide from ferromanganese slag instead of from the ore would depend upon the above factors viz. the slag constituents, sulphuric acid consumption and the filtration of leached and purified solution. With these objectives in view, this investigation was taken up and a low manganese slag and a high manganese slag have been studied.

Experimental

The granulated low manganese s ag was ground to two different mesh sizes viz -100 and -200 BSS to examine the fineness to which the granulated slag has to be ground for the maximum recovery of manganese. High manganese slag was not granulated and the crystalline lumpy slag was ground to -100 mesh only. The ground slags were leached in dil. sulphuric acid solution in excess over stoichiometric equi valent to contained manganese in the slag under agitation for 30 minutes at room temperature. After 30 minutes leaching, the leached solution was filtered and neutralised to a pH value of 6-7 with ammonia in the case of EMM and lime in the case of EMD. The neutralised solution was oxidised by blowing air for about an hour for precipitation of iron, aluminium and silica. The manganese sulphate solution so obtained was filtered and its purity was examined for production of EMD/EMM.

Experimental results and discussion

Analysis of the representative samples of the two slags used in the investigation are given in Table 1.

TABLE-1

Constituents %	Low Manga- nese Slag	High Manga- nese Slag		
Total Manganese	24.11	36.66		
Total iron	0.55	0.87		
Manganese as MnC) —	47.33		
SiO ₂	20.76	26.00		
Al ₂ O ₃	20.86	7.83		
CaO	16.80	5.04		
MgO	8.80	3.68		
BaO	2.21			
S		0.41		
Ρ	_	0.02		
Ground to -10	00 & - 200 BS	S -100 BSS		

Low Manganese Slag

Recovery of manganese on leaching the slag in the cell effluent from EMM cells containing 36 g/L sulphuric acid and 100% excess over the stoichiometric equivalent to contained manganese is given in Table 2.

It can be seen from Table 2 that a recovery of 72% manganese is obtained at the leaching stage with 100% excess acid in the spent liquor over the stoichiometric equivalent to contained manganese in the slag with the granulated slag ground to—100 mesh. This recovery of 72% increases to 80% when the slag is ground to -200 mesh. With -100 mesh and with 36 g/L of sulphuric acid in the spent liquor, about 20% of the slag was found to settle unreacted at the bottom together with the residual sludge containing Calcium sulphate, barium sulphate, aluminium silicate etc. It is hence seen that grinding to finer size (-200 mesh) is essential

TABLE-2

Recovery of manganese by leaching the low manganese slag with spent liquor from electrolytic manganese cells

	With 100% excess acid in the cell effluent over the stoichiometric equivalent to contained manganese	
Average percentage recovery	With slag ground to —100 Mesh	With slag ground to —200 Mesh
Manganese recove red in the leached solution	72%	80%
Unreacted manga- nese in the slag	20%	12%
Manganese lost in the sludge	4%	4%
Manganese lost in solution handling and filtration	4%	4%

TABLE-3

Recovery of manganese from the High Manganese Slag on leaching and purification

At the various stages of leaching & purification	Excess of sulphuric acid in the leaching spent liquor over stoichiometric equivalent to con- tained manganese (-100 Mesh BSS)	
	13%	65%
Leaching stage		
Recovered manganese in the leached solution after leaching	86%	95%
Manganese unrecovered in the leached residue	11%	4%
Manganese lost in solution handling & filtration	3%	1%
Purification stage		
Manganese recovered in the purified solution after precipitation of iron, aluminium and silica, etc.	, 77%	76%
Manganese lost in the precipitate twice washing with cold water	2%	8%
Manganese lost in solution handling & filtration	7%	11%

for maximum recovery of manganese from the slag.

High Manganese Slag

On the other hand, with high manganese slag and an excess of 37 and 65% sulphuric acid over the stoichiometric equivalent to contained manganese, recoveries of manganese obtained at the leaching and purification stage are given in Table 3.

Discussion of results

It can be seen from Table 3 that a recovery of 86% manganese is obtained at the leaching stage with 37% excess acid in the spent liquor on the stoichiometric equivalent to contained manganese in the slag. This recovery of 86% increases to about 95% with 65% excess acid. With increasing acid content in the spent liquor, higher recovery of manganese can be obtained; but at the same time the alumina and silicate going into the leached solution increase more than double-fold. With increasing alumina and silicate going into the leached solution, the quantity and volume of the precipitate during purification stage also increase uniformly. Further the high silicate and alumina in the slag, when go into solution, tend to form a gel which creates filtration difficulties. Because of these, the final recovery of manganese after the precipitation stage of iron, aluminium and silica, with 65% excess acid in the spent liquor also, falls down to 76-77% of the total manganese contained in the slag.

Though the recovery of manganese at the leaching stage may be very high, if the precipitate during iron, aluminium and silica precipitation is much, a good amount of manganese would be entrapped with the gelatinous precipitate, bringing down the recovery of manganese at the the final stage. It can be seen from Table 3 that about 8% of manganese is lost with the precipitate.

It would be advisable to remove as much of the undesirable constituents, such as iron,

aluminina, silica, etc. as possible at the leaching stage itself rather than taking them into solution and then precipitating again. Hence it is felt that an acid content which is about 35-37% in excess over the stoichiometric equivalent to the contained manganese would be preferable for the final optimum recovery of manganese from the high manganese slag.

Percentage of other constituents going into the leach solution at different concentrations of sulphuric acid in the leaching liquor over stoichiometric equivalent to contained manganese as % of their respective total content in the slag is presented in Table 4.

TABLE-4

Percentage of other constituents going into the leach solution as % of their respective total content in the slag

Name of the constituent going into leached solution	Low Manganese Slag (-200 Mesh)	High Manganese Slag. sulphuric acid in excess 37% 65%		
Iron	45%	55%	55%	-
Aluminium	35%	27%	62%	
Silica	26%	20%	52%	
Magnesium	62%	44%	54%	
Calcium	Trace	Trace	Trace	
Barium	Trace	Trace	Trace	

It can be seen from Table 4 that practically all the calcium and barium present in the slag are found in the residual sludge after leaching and goes into solution upto its limit of solubility. Good percentages of aluminium, silicate and magnesium enter the leaching solution together with iron. Iron, aluminium and silicate could be completely precipitated out during the iron purification stage. Magnesium over 8 g/L has deleterious effect in the operation of the electrolytic manganese metal cell and it cannot be allowed to build up. When it builds up, a part of the electrolyte has to be withdrawn each time and the magnesium removed as complex crystals of manganesemagnesium-ammonium sulphate.

TABLE—5 Consumption of sulphuric acid by the various constituents of the slag

	% sulphuric acid consumed		
Constituents	Low Manganese	High Manganese Slag	
	Slag (-200 Mesh)	37% excess	65% excess
Manganese	38	62.6	57.2
Calcium	28	6.84	6.23
Barium	1	-	
Aluminium	19	6.78	13.09
Magnesium	14	4.39	4.46
Iron	-	0.93	0.78
Silicate	—	9.40	9.65
Others		7.15	3.89
Balance left			
unreacted		1.9	4.7

Table 5 shows the consumption of sulphuric acid by the various constituents in the slag.

With low manganese slag, the whole of the decomposed calcium consumes sulphuric acid and precipitates out as calcium sulphate. Next to manganese, it can be seen that the acid consumption by calcium alone is in the order of 28%. Aluminium and magnesium come next to calcium in the consumption of acid.

With high manganese slag and 37% excess acid in the leaching spent liquor, as can be seen from Table 5, 63% of the acid contained in the solution is consumed by manganese, calculated on the basis of recovered manganese in the leach liquor, and 35% is lost in side reactions. With 65% excess acid, 57% is consumed by manganese and 38% is lost in side reactions. That means, 1.3 times more acid is lost in side reactions with 65% excess acid than with 37% excess acid. This also shows keeping the excess acid at about 37% as optimum.

Conclusions

With low manganese slag, it is seen that a recovery of 80% of contained manganese is obtained on leaching with 100% excess acid

with the granulated slag ground to -200 mesh. Under these conditions, only about 38% of the acid is consumed by manganese and the rest is lost in side reactions. In short, to take one tonne of manganese into solution from the slag, about five tonnes of acid is required. Electrodeposition of one tonne of manganese from its solution regenerates only 1.8 tonnes of acid. That is, about 3 tonnes of acid is additionally required for every tonne of manganese produced from the slag. This extra cost for sulphuric acid alone is likely to make production of manganese metal from the low manganese slag uneconomic compared to production of manganese from manganese ore in India.

On the other hand, with high manganese slag at 37% excess sulphuric acid, about 3 tonnes of sulphuric acid is required to take one tonne of manganese from the slag into solution. Taking into account the 1.8 tonne of acid generated, about 1.2 tonne of acid is required for production of 1 tonne of manganese metal which is comparable to the acid consumption with low or medium grade manganese ore.

For production of electrolytic manganese di-oxide, potassium as it builds up in the leach solution is deleterious. Hence, even high manganese slag is not recommended for production of EMD unless its potassium content is less than 0.08%.

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