Production of Silicomanganese Alloy from Low Manganese Containing Leached Sea Nodules Residue

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ABSTRACT

Leached sea nodules residue was used for the present study for exploring its utilization. The residue generated in ammoniacal-SO₂ pressure leaching was water washed to reduce the sulphur content. To improve the Mn/Fe ratio in the residue, it was blended with Fe-Mn slag or Mn ore in the calculated amount and smelting was carried out in 50 kVA submerged arc furnace. Various parameters such as holding time, amount of reductant, power input etc. were investigated. The maximum recovery of Mn from residue blended with Fe-Mn slag and Mn ore was 58% and 65% respectively in the form of silicomanganese.

KEY WORDS: Sea nodules; Sea nodule leach residue; Characterisation; Blending with Mn containing materials; Smelting; Silicomanganese; Submerged arc furnace

INTRODUCTION

The most extensive deposit of manganese oxides are found in the world’s oceans, which is known as polymetallic sea nodules or deep-sea manganese nodules or ferromanganese nodules that are 0.5–25 cm in diameter, with an average diameter of ~4 cm. Polymetallic sea nodules are also important resource of strategic metals like copper, nickel and cobalt. Several processes have been developed in various parts of the world to recover these metals (Xueyi et al, 1997; Agarwal and Goodrich, 2003), although none of them is in the stage of commercially exploitable, may be due to some mining and environmental hurdles (Manickam et al., 1996). In India, a pilot plant for the treatment of polymetallic nodules to recover copper, nickel and cobalt was set up at Hindustan Zinc Limited, Udaipur by Ministry of Earth Sciences, Govt. of India (Mittal and Sen, 2003). This is based on the Ammoniacal pressure leaching in presence of sulphur dioxide (Das et al, 1998; Das et al, 1999; Das, 2001). This process generates huge amount of residue (70-75% of treated nodules) after leaching of Cu, Ni & Co from the nodules. The leached residue mainly contains manganese, iron and silicon along with some quantity of lime, magnesia, alumina etc. The leached residue may be subjected to smelting along with reductant and flux in a submerged arc furnace to produce ferrosilicomanganese alloy (Tolsozguzov et al 1995; Rusakov et al, 2004), which is widely used during steel making. This will also improve the economics of the polymetallic sea nodules processing.

Although the Mn/Fe ratio (2.5) in leached residue is not favorable to process it directly to produce standard grade ferrosilicomanganese alloy (Narayanan and Subramanyam, 1959), it can be blended with a high manganese containing material to get the desired Mn/Fe ratio. Residue also contains considerable amount of sulphur due to leaching of the of sea nodules in ammoniacal-SO₂ medium. The metal sulphates decompose at higher temperature during smelting leading to evolution of SO₂ gas. In the reducing atmosphere of reduction smelting, SO₂ reduces and sulphur is transferred to the slag which is eventually transferred to the alloy phase (Turkdogan, 1983). High sulphur in ferrosilicomanganese may be detrimental for using it in steel making process. Therefore, sulphur needs to be removed from leached residue prior to smelting. In the silicomanganese smelting, the overall efficiency of the process depends upon the MnO reduction in the melt whether the raw material is high grade ore or low grade material such as leach residue. In leach residue, manganese is mainly in the form of Mn₂O₃. The reduction of Mn₂O₃ is much easier than MnO as MnO requires higher reduction potential (Habashi, 1997). The kinetics of the MnO reduction by carbon and the effects of different parameters have been studied by several investigators (Yastreboff et al, 2003; Shimpoo et al, 1984; Daines and Pehlke, 1971). The basic reactions pertaining to silicomanganese from leach residue smelting are (Habashi, 1997):

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\begin{align*}
\frac{1}{2} \text{Mn}_2\text{O}_3 + \frac{1}{12} \text{C} & \rightarrow \frac{1}{3} \text{Mn}_3\text{O}_4 + \frac{1}{12} \text{CO}_2 \quad (1) \\
\frac{1}{3} \text{Mn}_3\text{O}_4 + \frac{1}{6} \text{C} & \rightarrow \text{MnO} + \frac{1}{6} \text{CO}_2 \quad (2) \\
\text{MnO} + \text{C} & \rightarrow \{\text{Mn}_{\text{alloy}} + \text{CO} \quad (3) \\
(\text{SiO}_2)_\text{h} + 2\text{C} & \rightarrow \text{Si(L)} + 2\text{CO} \quad (4)
\end{align*}
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