

A PROCESS FOR RECOVERY OF IRON FROM COPPER SLAG

FIELD OF THE INVENTION

The present invention relates to a process for recovery of iron from copper slag. This invention particularly relates to a process for recovery of iron from a waste like granulated copper slag generated during the production of copper from its ores by a pyrometallurgical method. The present invention will be useful for solving the ecological and environmental issues with an added economic advantage of utilising the dump slag generated in the copper plants.

BACKGROUND OF THE INVENTION

Generation of waste (solid/liquid/gases) in varying amounts is a part of almost every metal casting industry. These wastes can be converted to wealth if processed for eventual recovery of valuables provided it is economical. Unsystematic disposal / dumping of these wastes may lead to environmental degradation and therefore, presently the reuse or recycling of the waste is often stressed upon. Copper smelter slag generated during the processing of copper concentrate for the production of copper is no exception. It is reported that for every tonne of copper metal production about 2.2 tonnes of slag is generated. Initial studies were carried out on physical and chemical characterisation and toxicological studies to decide about the waste management practice for granulated and slow cooled slag of the copper plant. Since the quantity of slag generated shall be accumulating thus requiring increased dumping space, the recovery of some of the value added product has been attempted.

Reference may be made to Yucel. et. al, [*Mineral Processing and Extractive Metallurgy Review*, 1992] wherein copper slag was reduced carbothermically recovering metals and an iron rich alloy. The alloy produced was processed hydrometallurgically for the recovery of copper, cobalt and disposal of Fe_2O_3 rich residue. Here the disadvantage is loss of the major metal values and the process is uneconomical with respect to the recovery of copper and cobalt. Reference may also be made to Topkaya [*ATB Metall*, 1990] wherein ancient copper slag of Kure in Turkey was subjected to carbothermic reduction to produce an Fe-Co-Cu alloy. It was found that with 4% coke powder addition an alloy containing 1.72% Co and 4.41% Cu could be obtained at 1400°C in 1h with Co and Cu recoveries of 97.7% and 86.7% respectively. Yucel et.al [*Scand. J. Metal*, 1999] reported the treatment of ancient Kure copper slag containing 2.38% cobalt and 3.51% copper by carbothermal reduction process in a DC arc furnace (open top) by adding coke with maximum metal recovery in one hour reduction time at a temperature between 1703-1753 K. In closed system recovery of cobalt

was 95.7 % and copper was 90% . Fluxing materials such as CaO and Al₂O₃ caused an increase in iron reduction but no appreciable influence on cobalt and copper recovery was noticed. Reference may also be made to Acma et.al [*Trans. Indian Inst. Met*, 1997 wherein copper slag generated at Kure, has been investigated for the recovery of copper and cobalt and production of magnet grade iron oxide by pyro-hydrometallurgical route. This fayalitic slag analysing about 0.8%Cu and 0.4%Co was reduced with coke/graphite in a DC arc furnace to yield a liquid alloy rich in iron and containing about 3.8% Cu, 3.3% Co and 2.1% S. Reference may be made to Jones et.al [*Int. Symp. challenges of process intensification ,Montreal,Canada*, Mintek paper No.8360, Aug 1996] wherein they reported the recovery of valuable metals, such as nickel, cobalt, and copper in an alloy from copper slags by carbonaceous reduction in a DC arc furnace. Pilot plant test work at Mintek (South Africa) has demonstrated recoveries of 98% nickel and 80% cobalt at the power levels of up to 600kW and maximum possible quantity of iron oxide in the slag. Reference may be made to Acma et.al [*Conf. Recycling of Metals, Dusseldorf /Neuss,Germany, 13-15 May, 1992*] wherein the slag has also been carbothermally smelted in a submerged electric arc furnace, partially reducing Fe to a metallic phase comprising of copper and other metals. The metallic phase has been transformed to the granules by passing through an air jet. The granule after grinding was leached with H₂SO₄ and the solution was purified with H₂S to separate CuS. After the co-precipitation step iron was precipitated as goethite from the final solution. From goethite through thermal decomposition, magnetic oxide was prepared.

Reference may be made to US patent 4,717,419, 1988, Makinen, et al. wherein the invention relates to a method for treating copper and nickel rich iron-bearing slags for the recovery of precious metals by reducing the slag by adding a sulphidizing agent. By means of controlled cooling, the precious metals are concentrated into the iron-base metal phase, where after the phase containing the precious metals can be separated by means of magnetic separation. A selective hydrometallurgical treatment was then carried out to recover the precious metals. Reference may also be made to US patent 4,349,383, 1982, Chaudhuri wherein, a copper bearing source is smelted into matte and a primary slag in a smelting process, and the matte is converted into blister copper and converter slag in a converter. The smelting is carried out under conditions of high oxygen potential to produce a matte and a primary slag both having relatively high copper contents. The primary slag and the converter slag are withdrawn and preferably mixed together, followed by reduction of both slags by means of gaseous reducing agents to produce additional amounts of copper and to render the slags virtually copper free. Reference may also be made to US patent. Nos. 596,705 (Hartenstein) 905,980 (Betts); 1,544,048 (Stout); 1,822,588 (Fowler et al); 2,653,868 (Lichty); 3,081,163 (Kuzell et al); 3,157,490 (Wiberg); 3,314,783 (Zimmerley et al)

and 3,857,700 (Ammann et al), wherein, Hartenstein patent discloses a process for utilizing the waste products of blast furnaces wherein slag is subjected to treatment with a carbonaceous material and electric current. The Betts patent discloses a metallurgical process wherein silicon is used in recovering iron and copper from a slag. The Stout patent discloses a method of treatment of copper metallurgical slag wherein the slag is treated with iron to extract additional copper. The Fowler et al patent discloses a process for recovering copper from slag wherein carbonaceous material is added to reduce the slag and obtain the copper therefrom. The Lichty patent discloses a process for recovery of metals from metallurgical slag wherein silicon is used as a reducing agent to obtain iron and copper from the slag. The Kuzell patent discloses a process of treating copper matte wherein iron and copper are recovered by air blowing a molten charge of the matte. The Wiberg patent discloses a method for refining metals. The Zimmerley et al patent discloses recovery of molybdenum from slag by means of a reduction smelting operation. The Ammann et al patent discloses a process for recovering copper from molten converter-type slags wherein the magnetite in the slag is reduced with carbonaceous materials and/or other solid reductants and stirring of the slag is utilized.

These above processes have, however, generally been relatively inefficient due to the difficulty of obtaining effective contact, i.e., wetting, between molten oxides, contained in molten slag, and solid reductants such as carbon.

The main object of the present invention is to provide a process for recovery of iron from copper slag.

Another objective of the present invention is to provide a process for the production of metal from the granulated slag generated during the processing of copper concentrates.

Still another object of the present invention is to provide a process for the production of metal from the granulated slag generated during the processing of copper concentrates from an Indian copper producing company.

Accordingly the present invention provides a process for the recovery of iron from copper slag which comprises:

- i. selecting and grinding the copper slag to the size in the range of 2-15mm,
- ii. mixing homogeneously copper slag, reductant and flux in the ratio range between 20:1:4 to 20:3:10.

- iii. creating molten pool of metal having carbon percentage in the range of 3-4.5 % in arc furnace by known method,
 - iv. inducting the mixture obtained in step (ii) in the molten metal pool at a slow rate so that vigorous reaction can be avoided,
 - 5 v. maintaining the temperature of the furnace in the range of 1350 to 1500°C for a period ranging between 1 – 3 hours,
 - vi. sprinkling reductant material into the molten bath so that foam can be avoided,
 - vii. tapping the melt from the furnace and casting by known method.
- 10 In an embodiment of the present invention, the copper slag used in the process may have the following composition range:

Cu(%)	: 0 - 0.523
Silica(%)	: 25-35
Lime(%)	: 3 – 10
Fe(%)	: 30-50
Cd(ppm)	: 0 - 0.005
Co(ppm)	: 2 – 6
Ni(ppm)	: 0 – 0.6
Pb(ppm)	: 2-10

- 15 In an another embodiment of the present invention, the reductant material may be selected from graphite, petroleum coke and like materials and may have size in the range between 0.2 to 10mm.

- In still another embodiment of the present invention, the addition of reductant material may be made through the following three stages:

- 20 stage-1: 15 to 20 weight % of the reductant is added initially after completely melting of metal pool,
- stage-2: 50 to 60 weight % of reductant is mixed with granulated slag and flux,
- 25 stage-3: 30 to 35 weight % of the reductant is added during the melting process to avoid foaming.

In yet another embodiment of the present invention the created amount of molten pool may be of 10 to 20 volume % of furnace capacity.

5 In still another embodiment of the present invention the flux used may be selected from oxide and carbonate of calcium and magnesium.

10 In still another embodiment of the present invention the obtained products may be grinding grade cast iron and like and the recovery rate of iron may be in the range of 75 to 85 weight % of iron values.

DETAILED DESCRIPTION OF THE INVENTION

15 In the process of the invention the copper slag from any copper industry is analysed for its chemical composition. The chunks of copper slag was broken into small lumps and ground into small granulated particles in the size range of 2 to 15 mm. Depending upon the form of iron oxide i.e. FeO , Fe_2O_3 , Fe_3O_4 and chemical composition of iron and silica in the copper
20 slag the amount of reductant and fluxing material is calculated. Granulated slag, reductant and the fluxes are mixed in a mixing miller for a time period of 2 to 5 min in order to get a homogenous mixture. In the arc furnace a molten metal pool bath was created and a calculated amount of reductant was added. To this molten pool the homogenous mixture
25 was added at a slow rate to avoid vigorous reaction. During melting a known amount of the reductant was sprinkled intermittently on the top of the melt to control the foaming action and material spillage. After complete melting slag was skimmed off and the metal was tapped in a ladle and poured in to a mould of desired shape by a known method.

30 Thus, the problems mentioned in the prior art are largely overcome, and the efficiency of reduction of the slags substantially improved. This procedure has been found to optimize utilization of the reductant by allowing its dispersion and dissolution in the molten metal bath before contacting and reacting with the molten slag at the molten metal-molten slag interface.

35 Novelty of the present invention is process for the preparation of value added products viz grinding grade cast iron using copper slag generated during the processing of copper concentrate which otherwise is considered as a waste. Other novel features of the inventions are creating a homogeneous mixture of slag, reductant and flux so that reaction kinetics is more than conventional process. The reductant is used in such a way so that maximum recovery of iron can take place.

The following examples are given by way of illustration and should not be construed to limit the scope of the invention.

Example-1

The granulated copper slag containing Cu(weight %): 0.523, Silica(weight %): 30.1, Lime(weight %) : 3.8, Fe(weight %): 42.8, Cd(ppm): 0.003, Co(ppm) :5.6, Ni(ppm): 0.58, Pb(ppm): 10.9 was selected from the copper slag generated during the processing of copper containing concentrate from a copper producing industry. 10 kg of granulated copper slag of size range 5 to 10 mm, lime of amount 2.5kg and graphite powder of amount 0.6kg was mixed in a muller for two minutes. 5 kg of pig iron was melted in direct arc furnace. In the molten pool, 0.2kg of graphite was added. Then the copper slag mixture was added slowly into the molten pool. The melt temperature was maintained at 1370 to 1390 °C and the reduction time was around 1 h. After complete melting, the slag was skimmed off from the furnace and the melt was tapped to a ladle and finally poured in moulds as well as in standard test blocks. Recovery of iron from the slag was about 85 weight %.

Example-2

The granulated copper slag containing Cu(weight %): 0.523, Silica(weight %): 30.1, Lime(weight %) : 3.8, Fe(weight %): 42.8, Cd(ppm): 0.003, Co(ppm) :5.6, Ni(ppm): 0.58, Pb(ppm): 10.9 was selected from the copper slag generated during the processing of copper containing concentrate from a copper producing industry. 15 kg of granulated copper slag of size range 10 to 15 mm, lime of amount 3.0kg and petroleum coke of amount 1.0kg was mixed in a muller for three min. 4kg of cast iron having carbon content 3.2 weight % was melted in direct arc furnace. 0.5kg of petroleum coke was added initially in the bath to which the copper slag mixture was added slowly. During melting 0.3kg petroleum coke was used for sprinkling to calm down the foam formation. The melt temperature was maintained at 1370 to 1390 °C and the reduction time was around 1.5 h. The melt tapping and pouring were same as in example one. The powder consumption for this operation was 50kWh. The casting so obtained was found to have a hardness of 37to 40 Rc.

Example-3

The copper slag containing Cu(weight %): 0.227, Silica(weight %): 30.9, Lime(weight %) : 0.41, Fe(weight %): 36.89, Cd(ppm): 0.003, Co(ppm) : 2.72, Ni(ppm): 0.37, Pb(ppm): 5.17 was selected from the copper slag generated during the processing of copper containing concentrate from a copper producing industry. 10 kg of copper slag of size range 5 to 10 mm, lime of amount 3.0kg and graphite powder of amount 0.5kg was mixed in a muller for two min. 4 kg of pig iron was melted in direct arc furnace. In the molten pool 0.3kg of graphite was added. Then the copper slag mixture was added slowly into the molten pool.

The melt temperature was maintained at 1390 to 1420 °C and the reduction time was around 1 h. After complete melting the slag was skimmed off from the furnace and the melt was tapped to a ladle and finally poured in moulds as well as in standard test blocks. Recovery of iron from the slag was about 75 weight %. Power consumption was found to be 40kWh.

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The main advantages of the present invention are:

1. The recovery of iron from the copper slag which was otherwise considered as a waste.
2. The produced alloy has the potential to be used as grinding media applications.
- 10 3. Copper slag acts as a alternative raw material for the production of alloyed cast iron compared to conventional one.
4. Recovery of iron is very high and is around 75 to 85 weight %.
5. Melting can be carried out in the open top or closed top arc furnace.
- 15 6. By this process any grade of copper slag can be used as a raw material for the recovery of iron.

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We claim:

1. A process for the recovery of iron from copper slag which comprises:

- i. selecting and grinding the copper slag to the size in the range of 2-15mm,
- 5 ii. mixing homogeneously copper slag, reductant and flux in the ratio range between 20:1:4 to 20:3:10.
- iii. creating molten pool of metal having carbon percentage in the range of 3-4.5 % in arc furnace by known method,
- iv. inducting the mixture obtained in step (ii) in the molten metal pool at a slow rate
10 so that vigorous reaction can be avoided,
- v. maintaining the temperature of the furnace in the range of 1350 to 1500°C for a period ranging between 1 – 3 hours,
- vi. sprinkling reductant material into the molten bath so that foam can be avoided,
- vii. tapping the melt from the furnace and casting by known method.

15 2. A process as claimed in claim 1 wherein the copper slag used in the process have the following composition range:

Cu(%)	: 0 - 0.523
Silica(%)	: 25-35
Lime(%)	: 3 – 10
Fe(%)	: 30-50
Cd(ppm)	: 0 - 0.005
Co(ppm)	: 2 – 6
Ni(ppm)	: 0 – 0.6
Pb(ppm)	: 2-10

3. A process as claimed in claims 1-2 wherein the reductant material are selected from graphite, petroleum coke and like materials and have size in the range between 0.2
20 to 10mm.

4. A process as claimed in claims 1-3 wherein the addition of reductant material are made through the following three stages:

25 stage-1: 15 to 20 weight % of the reductant is added initially after completely melting of metal pool,

stage-2: 50 to 60 weight % of reductant is mixed with granulated slag and flux,

stage-3: 30 to 35 weight % of the reductant is added during the melting process to avoid foaming.

- 5 5. A process as claimed in claims 1-4 the created amount of molten pool is of 10 to 20 volume % of furnace capacity.
6. A process as claimed in claims 1-5 wherein the flux used are selected from oxide and carbonate of calcium and magnesium.
- 10 7. A process as claimed in claims 1-6 wherein the obtained products is grinding grade cast iron and like and the recovery rate of iron is in the range of 75 to 85 weight % of iron values.