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# Recovery of germanium and other valuable metals from zinc plant residues

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**Abstract**

The main purpose of this study was to characterize and to extract germanium from the copper cake of Çinkur Zinc Plant. The physical, chemical and mineralogical characterization of the ground copper cake sample obtained from Çinkur showed that it was 84% below 147 µm containing 700 ppm germanium. The copper cake also contained 15.33% Cu, 15.63% Zn, 1.66% Cd, 1.33% Ni, 0.64% Co, 0.35% Fe, 2.62% Pb, 12.6% As, 0.18% Sb and 3.42% $SiO_2$. The mineralogical analysis indicated the complex nature of the copper cake which was mainly composed of metallic and oxidized phases containing copper, arsenic, zinc, cadmium, etc. The sulfuric acid leaching experiments were performed under the laboratory conditions. The optimum collective extraction of germanium and other valuable metals was obtained at a temperature range 60 to 85 °C for a leaching duration of 1 h with sulfuric acid concentration of 150 gpl and using a solid–liquid ratio 1/8 g/cc. Under these conditions, the recovery of germanium was 92.7% while the other metals were leached almost completely. The optimum selective leaching conditions of germanium was determined as half an hour leach duration, 1/8 g/cc solid–liquid ratio, 100 gpl sulfuric acid concentration and a temperature range 40 to 60 °C. Under these conditions the leach recovery of germanium was 78%. The dissolution's of other metals like cobalt, nickel, iron, copper, cadmium and arsenic were almost low. So, germanium would be separated more selectively at the following precipitation by tannin stage.


*Keywords:* Copper cake; Germanium; Sulfuric acid leaching

## 1. Introduction

None of the germanium minerals is mined solely for its germanium content. All of the germanium recovered worldwide is a by-product of other metals, mostly zinc, copper, and lead. In electrolytic zinc plants which are becoming increasingly important for environmental reasons, germanium is separated chemically during the purification of the electrolyte prior to electrolysis. Germanium is one of several impurities that have an adverse effect upon zinc electrolysis. If the germanium concentration is high enough in the separated solids, economic recovery is possible (Thompson and Musgrave, 1952). Wardell and Davidson (1987) have made an extensive research on leaching behaviour of zinc processing residues that contain an average of 0.46% germanium. The results obtained suggested that the

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roasting procedure prior to leaching with $H_2SO_4$, and $SO_2$ has altered the form of germanium and made it more amenable to leaching.

Essentially, all hydrometallurgical germanium recovery processes involve getting the germanium into the solution and the treatment of pregnant leach solution with various chemicals in order to extract the germanium values from the solution selectively. Thus, two important topics are discussed below concerning the recovery of germanium from leach solutions; solvent extraction, and precipitation. The selection of the most suitable technique depends highly on the type of the solution, i.e., concentration of germanium in the solution and other constituents of the solution. Generally, the input to solvent extraction is a leach solution containing relatively high concentrations of germanium (i.e., 1 gpl Ge). But KELEX-l00 was found promising even at relatively lower germanium concentrations (i.e., 0.2–0.3 gpl). On the other hand, tannin precipitation would be employed to treat those solutions with much lower concentrations of germanium (Zhov et al., 1989).

Chemical precipitation methods are used to treat the leach solution containing relatively low concentrations of germanium, i.e., less than 1 gpl (Seifullina et al., 1973). Those chemical substances making strong compounds with germanium are added to the pregnant leach solution and germanium is precipitated in the form of insoluble complexes. Tannin (glucosides of tannic acid of varying composition, generally containing 50–80% tannic acid) is generally employed for leach solutions containing very low concentration of germanium while for higher concentrations $H_2S$ and Zn are preferred. The pertinent reaction for tannin precipitation of germanium can be written as;

$$Ge^{+4} + O_2 + H_6T \rightarrow GeO_2{*}H_6T$$

Where T represents the Tannic Acid ($C_{14}H_{10}O_9$) with molecular weight of 322.20 (Zelikman, 1966).

After the precipitation is complete, the germanium–tannin compound is filtered and collected. The efficiency of this process varies between 78 and 100%. On the other hand, upon addition of tannin, the solution becomes contaminated whereby creating problems in the following zinc electrolysis. In addition to tannin; $H_2S$ and zinc, MgO and $Ca(OH)_2$ can also be used in order to precipitate germanium from leach solutions (Hoffmann, 1991).

World production of germanium, which is used widely in the chemical, electronic and optical materials industries, estimated by the U.S. Geological Survey to be 100 metric tonnes in 2006. It is obtained mainly as a by-product of the extraction of other metals, and zinc smelter flue systems are the principal source. Çinkur zinc plant in Kayseri, Turkey produced electrolytic zinc requiring the leach solution to be purified prior to electrolysis from the impurities such as, Co, Ni, Cd, Ge, Cu, etc. Therefore solution purification was done by precipitation in two step; cobalt and nickel were removed from leach solution by using $CuSO_4.5H_2O$, $As_2O_3$ and zinc powder in the first step, the filtercake obtained from first step called as cobalt cake in literature, and cadmium was precipitated by $CuSO_4.5H_2O$, $Sb_2O_3$ and zinc powder in the second step and this precipitate called as cadmium cake. In fact, there are three types of zinc plant residues (ZPR) in the literature; iron cake, copper cake and cobalt cake. Generally, germanium is concentrated at iron filter cake (first step purification cake), and thus recovered from this residue. But all of the filtercake obtained from solution purification steps was stockpiled in the same area as a mixture in Çinkur zinc plant, and this ZPR is called as copper cake due to its high copper content (15.33% Cu). In connection with this, the residues from the solution purification section are the richest source of germanium at Çinkur. Çinkur has been stockpiling solution purification residues at its zinc plant in Turkey and has built up a stock of more than 300 t with a germanium concentration in excess of 700 ppm (Baytekin, 1983). But nowadays, this plant produces only clinker due to economic reasons, whereas it will produce electrolytic zinc in next future.

In this study the possibility of recovery of germanium and the other metal values (Cu, Zn, Cd, etc.) from Çinkur solution purification precipitates (copper cake) has been studied. The first step in the metals recovery experiments was the characterization and sulfuric acid leaching of copper cake samples. After obtaining the pregnant leach solution with the optimum leach recoveries, the solution was treated by tannin in order to recover germanium by precipitation. The optimum precipitation conditions with tannin were determined by this study. But the results of precipitation of germanium by tannin from pregnant leach solution of copper cake will be given in next paper. On the other hand, the metal values other than germanium could be precipitated by zinc dust or scrap iron while the remaining solution could be advanced to leaching unit or to the electrolysis unit.

## 2. Experimental

### 2.1. Materials

The copper cake obtained from Çinkur in ground form was characterized physically, chemically and mineralogically. The dry