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Recovery of Selenium from Scrubber Sludge in Copper Process

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Abstract : The sulphur dioxide gases generated as a by-product of smelting and converting operations of copper concentrate contain selenium apart from zinc, lead, copper, cadmium, bismuth, antimony, and arsenic. The gaseous stream is treated in waste heat boiler, electrostatic precipitator and scrubbers to remove coarse particulate matter in order to produce commercial grade sulfuric acid. The gas cleaning section of the acid plant uses water to scrub the smelting gases. After scrubbing, the sludge settled at the bottom of the scrubber, was analyzed in present investigation. It was found to contain 30 to 40 wt% copper and selenium up to 40 wt% selenium. The sludge collected during blow-down is directly recycled to the smelter for copper recovery. However, the selenium is expected to again vaporize due to high oxidation potential during smelting and converting, causing accumulation of selenium in sludge. In present investigation, a roasting process has been developed to recover the selenium before the copper recovery from the sludge at smelter. Selenium is associated with copper in sludge as copper selenide, as determined by X-ray diffraction and electron microscopy. The thermodynamic and thermos-gravimetry study revealed that the copper selenide phase present in the sludge was amenable to oxidation at 600°C forming oxides of copper and selenium (Cu-Se-O). However, the dissociation of selenium from the copper oxide was made possible by sulfatation using sulfur dioxide between 450 to 600°C, resulting into the formation of $CuSO_4$ (s) and SeO_2 (g). Lab scale trials were carried out in vertical tubular furnace to determine the optimum roasting conditions with respect to roasting time, temperature and molar ratio of O_2:SO_2. Using these optimum conditions, selenium up to 90 wt% in the form of SeO_2 vapors could be recovered from the sludge in a large-scale commercial roaster. Roasted sludge free from the selenium and containing oxides and sulfates of copper could now be recycled in the smelter for copper recovery.

Keywords : copper, selenium, copper selenide, sludge, roasting, SeO_2
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