THE EXTRACTION OF GALLIUM AND GERMANIUM FROM ZINC OXIDE.

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When zinc ores containing germanium and gallium in minute amounts are smelted these elements, being less volatile than zinc, tend to remain in the retort residues. The oxide of zinc prepared from these residues is therefore a good source for gallium and germanium, since it contains them in a comparatively concentrated form. However, it appears that the produce from the same type of ore, while being fairly uniform so far as the germanium is concerned, may possess a very varying gallium content. This was indicated by the fact that a 100-pound sample gave 8 g. of practically pure gallium, while 200 pounds received at a later date from the same source showed only mere traces. The quantity of germanium in both samples was almost identical.

The above mentioned elements were extracted in the following manner: One kg. of zinc oxide was treated with 2400 cc. of commercial hydrochloric acid in a large flask. Portions of the oxide were added at a time to prevent caking. When all the oxide had dissolved, a little potassium chlorate was carefully added until, after vigorous shaking, oxides of chlorine were evolved. The flask was then quickly connected to a condenser, and the solution distilled with a thermometer dipping into the liquid. A battery of several flasks was kept running.

Each flask was heated by 3 burners applied directly to the glass. Pyrex flasks were found to be very suitable, since the insoluble lead chloride did not cause breakage.

The distillate was collected in two portions; the first receiver being changed as soon as the distillate gave a fairly good precipitate with hydrogen sulfide. With the thermometer dipping into the liquid and with the oxide and acid in the proportions given above, the temperature at which the germanium began to distill was about 121°. This point was found to vary with the type of oxide employed and also with the ratio of acid to oxide. The smaller the quantity of acid used, the higher the temperature at which the germanium began to come over. When the thermometer reached 135–140° the distillate was usually found to give practically no sulfide precipitate.

The liquid collected below 121° when treated with hydrogen sulfide turned first brown and then gave a minute yellowish precipitate. The fraction collected above 121°, which contained nearly all the germanium, was thoroughly saturated with hydrogen sulfide and allowed to stand for some time. The white sulfide was then filtered off and placed aside for future work.

The flask containing the residue was disconnected, a liter of water added to the concentrated chlorides, and the whole poured into a large earthenware vessel. After the lead chloride had settled, the liquid was decanted into an enamelled pail and treated with ammonium hydroxide until a slight permanent precipitate formed. The whole was then digested with zinc for several hours at the boiling point, all evaporated water being replaced. The precipitation of the gallium was considered complete when some of the supernatant liquid gave a precipitate of basic zinc chloride upon the addition of water. The metals and basic salts were removed by filtration. The equivalent of 3 kg. of the original oxide was treated in each pail. This step as well as every succeeding step was checked by means of the spectroscope to insure the complete removal of gallium in every case.

The operation described above gave a comparatively large quantity of concentrate, and since this was supposed to contain less than 1% of gallium, it was thought best to repeat the concentration after the removal of the tin and copper groups.

It was found convenient to employ about 10 of the first precipitates. These were dissolved in commercial hydrochloric acid with the aid of a little potassium chlorate, and the solution boiled to expel the oxides of chlorine, after which it was allowed to stand for some time. The insoluble lead chloride was removed by filtration and the filtrate thoroughly saturated with hydrogen sulfide to remove the greater portion of the elements of the tin and copper groups. The liquid was filtered, the filtrate boiled to expel hydrogen sulfide and neutralized with dil. ammonium hydroxide until a permanent precipitate just formed. The solution was then digested at the boiling point with zinc. When the solution had turned basic it was diluted somewhat and filtered. The operation was repeated until the basic precipitate failed to give the gallium line. The precipitates which were poor in gallium being placed with those obtained during the first concentration from the crude zinc chloride.

The precipitates which were rich in gallium were again dissolved in commercial hydrochloric acid, the solution nearly neutralized, saturated with hydrogen sulfide as before and the liquid filtered. This time only a small precipitate formed, consisting mainly of cadmium sulfide. The filtrate was treated with a quantity of ammonium chloride, made alkaline to litmus by the addition of ammonium hydroxide, and then boiled until just acid. The gelatinous precipitate consisting of gallium, aluminum and iron hydroxides was filtered off and washed as thoroughly as possible.

The foregoing processes were repeated until about 100 pounds of the original zinc oxide had been worked up with a yield of 60 g. of the crude hydroxides.

The crude hydroxides were dissolved in the minimum quantity of hydrochloric acid by boiling, diluted with water and nearly neutralized with sodium hydroxide solution. The liquid, after the addition of a little formic acid, was treated with a slight excess of sodium formate, and the precipitate filtered off and washed thoroughly to insure complete removal of zinc. The filtrate gave a faint gallium line indicating that the precipitation of gallium was not complete.

The precipitate and filter paper were removed to a casserole, stirred with water and thoroughly saturated with hydrogen sulfide. A quantity of 1% hydrochloric acid was added and after standing for some time, the insoluble tin and cadmium sulfides were removed by filtration. Since the filtrate was too large in volume to work with, the gallium was precipitated by making the liquid slightly alkaline with ammonium hydroxide and boiling until faintly acid to litmus. The gallium and aluminum hydroxides were separated by filtration, dissolved in the minimum quantity of hydrochloric acid, and an excess of sodium hydroxide solution added. By electrolizing with a current of 1.5 amperes, using platinum electrodes of about 3 sq. cm., the gallium was deposited on the cathode in extremely bright globules which dropped off as they became larger.

When the gallium ceased to be deposited, the solution was removed and the metal washed several times with water, and the globules then united by the addition of a drop or two of conc. hydrochloric acid. The latter was immediately removed by washing with water and finally with alcohol.

Any gallium remaining in the liquid and wash waters, after electrolysis, was regained by precipitating in the usual manner as the ferrocyanide from a strongly (hydrochloric) acid solution.

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SELENIC ACID AND COPPER SELENATE.[1]

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This article deals with the extraction of selenium from smelter fluedust and from anode slime; the preparation of pure selenium dioxide and selenious acid; the preparation of pure selenic acid; the detection of selenious acid present in selenic acid, and the detection of sulfuric acid present in selenic acid; attempts to prepare perselenates; the hydrates of copper selenate, and the ammonates of copper selenate.

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by Joseph Peter Koller in partial fulfillment of the requirements for the degree of Doctor of Philosophy.