26. *Gallium. Part VI. The Separation of Gallium and Germanium from Alkaline Extracts of Germanite by Electrolysis.*

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Direct electrolysis of the alkaline extract of germanite yields a mixed deposit of gallium and germanium metals which is easily separated, yielding pure gallium and germanium tetrachloride. Yields of over 80% are recovered directly in this manner, the remainder being recovered from the spent electrolyte and from the cathodic gases. This method of extraction is considerably simpler and more efficient than any previously described.

THE advantages of alkali digestion as a means of separating both gallium and germanium from the greater bulk of copper and iron sulphides in germanite ore have already been reported by Sebba and Pugh (J., **1937**, 1371), who have also described a chemical method of isolating pure gallium and germanium dioxide from the alkali extract. The chief advantages of the method are comparative simplicity and high yields : the yields of both metals in actual extractions were considerably higher than had ever been reported in the mineral. Subsequently (J., **1937**, 1373), the same authors described the conditions for the successful electrodeposition of pure gallium from alkaline solutions. The latter work immediately suggested the possibility of the direct separation of gallium by electrolysis of the alkali extract of the mineral. This would have the merit of great simplification because, in the chemical method already referred to, the major part of the work is concerned with the removal of impurities before the gallium is electrolysed out.

Though it has not been found possible to isolate gallium alone in this way, it is possible to obtain a mixed deposit of gallium and germanium metals from which pure gallium and germanium tetrachloride or dioxide can easily be obtained. The deposit is entirely free from arsenic, and this simple process of electrolysis, therefore, separates completely one of the most troublesome elements associated with gallium and germanium. The only impurities are traces of molybdenum, antimony, and lead.

However, as shown by Sebba and Pugh (*loc. cit.*), it is not possible to recover gallium completely by electrolysis of alkaline solutions; and Schwartz, Heïnrich, and Hollstein (*Z. anorg. Chem.*, 1936, **229**, 159) have shown that the same applies to germanium. Under the conditions to be described, it is shown that recoveries of the order of 80—85% of both metals are possible. The remainder may be recovered by chemical means, or the spent electrolyte may be used for the extraction of a fresh portion of the mineral. If the chemical method is adopted, the presence of arsenic in the liquor does not complicate the separation of gallium because the arsenic is in the reduced condition.

During electrolysis a small proportion of the germanium is volatilised as hydride, and this may be recovered by decomposition in a heated tube.

EXPERIMENTAL.

Extraction of Gallium and Germanium.—The separtion of the two metals from 1 kg. of ore was carried out by the method already described by Sebba and Pugh (*loc. cit.*); the main alkaline filtrate (1½—2 l.) was electrolysed directly, after removal of any crystals of sodium trioxysulpharsenate which separated. (The original washings were not added to the main filtrate but used for the extraction of a second portion of ore.)

Choice of Electrodes.—Platinum was not very satisfactory as a cathode, chiefly because of the difficulty of removing the deposit, which adhered strongly, and because chlorination was subsequently found to be the best means of dealing with the mixed deposit. Copper and nickel were both satisfactory. The deposit adhered well and was easily removed afterwards by bending, whereupon it cracked and flaked off. Hall and Koenig (*Trans. Electrochem. Soc.*, 1934, **65**, 215) have described the use of copper for the electrodeposition of germanium from alkaline solution. Tin was found to be useless because it became too brittle after a few hours' use.

As anode, platinum was certainly the best, but nickel was also satisfactory. Nickel anodes suffered a loss of approximately 0·2% in weight after 100 hours' use. Nickel was never found in the cathodic deposit.

Temperature.—Hall and Koenig (*loc. cit.*) recommended temperatures of 70—80° for the electrodeposition of germanium from alkaline solutions, but we found temperatures of this order quite unsuitable because the deposit was loose and non-adherent, and some gallium melted off and dropped back into the bath, where it redissolved. At 25—35° the deposit was hard and adherent. No external heating was necessary to maintain these temperatures.

Current Density.—In most of the experimental work, the cathode was a sheet of copper 6 cm. long and 5 cm. wide. The nickel anode was about twice this size. The cell carried a current of 1—1·5 amps. at 3—4 volts, giving a C.D. at the cathode of 0·016—0·025 amp./cm.^{2}, depending on the concentration of the electrolyte. In the actual extraction method worked out, the electrodes were about four times the above sizes, and electrolysis was carried out at 12—15 volts with a current of 4—5 amps.

Effect of Concentration.—Varying the concentration of alkali in the electrolyte had little or no effect either on the rate of deposition or on the nature of the deposit. Good results were obtained from solutions that were 6N with respect to sodium hydroxide, and this was approximately the concentration of the alkali extract of the ore. The factor which determined the rate of deposition, the efficiency of recovery, and the physical nature of the deposit was the concentration of gallium and germanium. The ratio of the concentration of these two metals in the ore and in the alkali extract was approximately 1 : 5.

Deposition of the metals became very slow when the concentration of gallium fell to 0·5 g./l.; on the other hand, when its concentration exceeded 5 g./l., although the rate of deposition was high, the initial deposit was soft and silvery and formed a poor base for further deposition. Gallium was deposited preferentially, for the deposit formed during the first few hours was generally soft and silvery in appearance, with evidence of globules of gallium, but as deposition proceeded, it became black, hard, and adherent. Analysis showed that the ratio Ga : Ge in the deposit formed during the first 3 hours was much higher than it was in the electrolyte.

The change in the rate of deposition of the mixed metal with time was a curious one. For the first 10 hours, when gallium was actively depositing, the rate was proportional to the concentration of the metals in solution; thereafter the rate fell off rapidly. This would indicate that the deposition voltage of germanium on gallium is lower than it is on germanium. Hall and Koenig (*loc. cit.*) reported that the deposition of germanium on copper ceases when the copper is coated with germanium and thereafter only hydrogen is evolved.

It was not possible to remove all the gallium and germanium by electrolysis under any conditions investigated, for the rate of deposition of germanium became so low after a certain point that loss of germanium as hydride was serious; on prolonged electrolysis, the cathode diminished in weight. The practical limit for successful deposition was reached when the concentrations of gallium and germanium had been reduced to 0·5 and 3 g./l., respectively, irrespective of the concentration of alkali in the solution.

In order to attain reasonable efficiency, therefore, it was necessary to employ solutions of relatively high concentration; but, as already noted, concentrations of gallium exceeding 5 g./l. gave unsatisfactory deposits. In practice, from 2 l. of extract containing 10 g. of gallium and 50 g. of germanium (from 1 kg. of ore) it was possible to obtain within 36—48 hours a satisfactory deposit of mixed metal consisting of 9 g. of gallium and 41 g. of germanium, representing over 80% recovery of both metals.

Recovery of Metals from Spent Electrolyte.—The spent electrolyte was most usefully employed for the extraction of a fresh portion of ore and this was repeated for a third portion. At this stage it became necessary to recover the metals by chemical means. Gallium was completely precipitated as hydroxide by neutralisation (pH 5), and germanium as dioxide by making the filtrate strongly ammoniacal. The precipitates were then added to a fresh alkali extract for electrolysis.

Treatment of Electrolytic Deposit.—The deposit dissolved only with difficulty. When finely powdered, it was readily attacked by hot concentrated nitric acid and by hot sulphuric acid, but in both cases, the action soon ceased because of deposition of a white coating of germanium dioxide on the metal surface. The effect of *aqua regia* was no better. Alternate treatment with acid and alkali eventually dissolved the metals. The best means of attack was chlorination. The coarsely powdered metal was placed in a hard-glass tube and heated in a current of chlorine, the vapours being condensed in a small distilling flask well cooled in a freezing mixture. A white residue of gallium oxide usually remained in the tube unless both the metal powder and the chlorine were thoroughly dried. This residue was washed into the receiver with a small quantity of concentrated hydrochloric acid. The distillate was then fractionated, germanium tetrachloride passing over at 78—80°. It was purified and treated by methods described by Dennis and Hance (*J. Amer. Chem. Soc.*, 1922, **44**, 304). The gallium chloride solution remaining was purified from traces of molybdenum, antimony, and lead by treatment with hydrogen sulphide in acid and in alkaline solution, and the gallium was finally recovered by electrolysis of alkaline solution as described by Sebba and Pugh (*loc. cit.*).

Recovery of Germanium volatilised as Hydride.—During the later stages of the electrolysis, when hydrogen evolution was considerable, there was much loss of germanium as hydride at the cathode, about 8—10% of it being thus lost. It was recovered by enclosing the cathode within a glass " bell " and leading the gases through a glass tube maintained at 350—400° in a tubular furnace (Muller and Smith, *ibid.*, p. 1909). Although this was effective in recovering every trace of germanium, the modification necessarily caused a considerable increase in the resistance of the cell and consequently a decrease in the rate of deposition. The black deposit was a mixture of germanium and arsenic. It was chlorinated and fractionally distilled in a current of chlorine. The details of the separation of germanium and arsenic have been adequately described (Dennis and Papish, *ibid.*, 1921, **43**, 2131).

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