

THE EXTRACTION OF GERMANIUM FROM  
CRUDE ZINC OXIDE

by  
Philip S. Clarke

Class of 1921  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
Pasadena, Cal.

## I. Purpose of Investigation.

Since the discovery of germanium in certain American zinc ores, notably that of Joplin, Mo., several procedures have been suggested for the extraction of the germanium. These procedures, however, were simple distillations of the zinc ore with hydrochloric acid carried out in the laboratory on a small scale. The cost of the materials and the character of the reagents required obviously would cause such procedures to be impracticable on a large scale.

In the present investigation, the reactions of germanium compounds and the actions of different reagents on the sample were observed with the view toward developing a method of extraction that would be applicable on an industrial scale. For this purpose, a ten-pound sample of germanium-bearing zinc oxide was furnished by the New Jersey Zinc Co. with the accompanying information that germanium was present in the sample to the extent of 0.25%  $\text{GeO}_2$ .

## II. Properties of Ge Compounds.

A list of the most important quadrivalent Ge compounds with their characteristic properties is given below:

$\text{GeF}_4$ - Formed by action of HF on  $\text{GeO}_2$ . Hydrated salt crystallizes and melts in own water of crystallization when heated moderately, forming a syrup.

$\text{GeCl}_4$ - Non-ionized liquid. Hydrolyzed by  $\text{H}_2\text{O}$  unless excess of HCl is present. When pure, boils at  $86^\circ \text{C}$ .

$\text{GeBr}_4$ - Non-ionized liquid. Hydrolyzed by  $\text{H}_2\text{O}$  vapor in air. Volatile, but to less degree than  $\text{GeCl}_4$ .

$\text{GeO}_2$  - White solid, soluble in water, and solubility rises with temperature. Tends to become colloidal. Aqueous solution reacts acid. Reduced by hydrogen or carbon to metal. Soluble in HCl and  $\text{H}_2\text{SO}_4$ , but not in  $\text{HNO}_3$ .

$\text{GeS}_2$  - White solid, soluble in  $\text{HNO}_3$ . Tends to form colloidal solution unless there is high H ion concentration present. Therefore precipitated from solutions of high H ion concentration only. Dissolves in  $\text{NH}_4\text{OH}$  to form

salt of thioacid. Aqueous solution soon decomposes into  $\text{GeO}_2$  and  $\text{H}_2\text{S}$ .

$\text{K}_2\text{GeF}_6$ - Soluble in water. (1 pt. in 180 pts.  $\text{H}_2\text{O}$  at  $18^\circ$ , 1 pt. in 35 pts.  $\text{H}_2\text{O}$  at  $100^\circ$ .) Is the K salt of a well defined acid  $\text{H}_2\text{GeF}_6$ . Gray-green gelatinous precipitate. Reduced by  $\text{H}_2$  to  $\text{GeF}_2$  and Ge.

### III. Former Methods of Extraction.

The procedures devised to extract Ge from crude ZnO were all distillations involving the dissolving of the charge in conc. HCl and distilling the Ge over as  $\text{GeCl}_4$ . Various reagents were used, such as chlorine gas,  $\text{KMnO}_4$ ,  $\text{K}_2\text{CrO}_4$ , or  $\text{KClO}_3$ , to oxidize the arsenic in the charge to the non-volatile  $\text{AsCl}_5$  and thereby prevent contamination of the distillate with volatile  $\text{AsCl}_3$ .

The method of extraction of A.A. Noyes is as follows: To 100 g. ZnO, add 200 cc. conc. HCl in a flask connected with a water-cooled condenser. Pass  $\text{Cl}_2$  into the mixture until  $\text{Cl}_2$  appears in the condenser receiver and then distil by boiling. Distil to about one-half volume. Dilute the distillate with an equal volume of water, and pass in  $\text{H}_2\text{S}$  for at least one-half hour. A white, voluminous precipitate

of  $\text{GeS}_2$  is obtained if Ge is present.

The procedures given by others are slight modifications of the above method.

#### IV. Experimental Work.

##### a). Qualitative Analysis.

The sample was analyzed by the system of analysis given by A.A. Noyes\*. The sample was found to dissolve completely in hot, dilute HCl. Since heating of the HCl solution might involve the loss of Ge as volatile  $\text{GeCl}_4$ , a 2 g. sample was distilled with an excess of HCl and the resulting residue and distillate both analyzed.

The residue was evaporated to dryness, then dissolved in 20 cc 6 N. HCl and 180 cc water and analyzed. The distillate was saturated with  $\text{H}_2\text{S}$  and the resulting precipitate was tested for As and Ge. The precipitates obtained in the detection of any metal were compared with corresponding precipitates obtained from solutions of known concentration of that metal in order to ascertain approximately the amount present.

A 2 g. sample was also analyzed for the acidic constituents by the procedures given in the same system of analysis as used above. The amounts of

\*Qualitative Analysis- 8th Revision.

each constituent were determined in the same approximate way as in the case of the basic constituents.

The results obtained are as follows:

Table I.

Basic		Acidic	
<u>Constituent</u>	<u>Amount</u>	<u>Constituent</u>	<u>Amount</u>
Pb	20 mg	S	10 mg
Cd	trace	SO <sub>4</sub>	30-40 mg
Al	80 mg	Cl	trace
Zn	princ. constituent		
K	10 mg		
Fe	trace		
As	3-4 mg		
Ge	5 mg		
Sr	trace		

The sample was later tested for gallium and indium. A trace of gallium was detected by making 200 cc of the HCl solution of the sample slightly ammoniacal, adding 1.5 g hydrated sodium sulfite, slightly acidifying with HCl and boiling for 6-7 minutes. After filtering the precipitate was dissolved in a few cc HCl, an equal volume of ether added and the solution saturated with HCl gas. The resulting precipitate of AlCl<sub>3</sub> was filtered off. The ether and excess of HCl were driven off from the filtrate by boiling and Ga again precipitated by sodium sulfite solution as before.

In the tests for indium strong NaOH solution was added to the solution of the sample until the zinc and aluminum hydroxides redissolved, a small amount further added, the solution boiled for a few minutes and filtered. The residue was washed and dissolved in HCl and precipitated again from NaOH solution as above. This second precipitate was dissolved in a few cc. of HCl and boiled almost to dryness. Indium was tested for in the spectro-scope using the solution obtained above. The characteristic line in the blue violet to the right of the Sr line was looked for, but was observed to be absent, showing absence of indium.

b). Quantitative Analysis.

Determination of Ge as  $\text{GeO}_2$ .

The fact that  $\text{GeS}_2$  is insoluble in the presence of sufficient mineral acid was utilized in an attempt to determine Ge quantitatively. A 10 g. sample was distilled with 50 cc conc. HCl and the arsenic and germanium in the distillate precipitated as sulfids by  $\text{H}_2\text{S}$ . The combined sulfids were filtered off and dissolved on the filter by a minimum quantity of  $\text{NH}_4\text{OH}$  without washing. The ammoniacal solution was warmed to  $85-95^\circ$  and acidified with acetic acid.

The  $\text{As}_2\text{S}_3$  reprecipitated by this treatment was filtered off and washed with hot water. The filtrate was saturated with  $\text{H}_2\text{S}$ , and while the gas was bubbled thru the solution, it was strongly acidified with an equal volume of conc.  $\text{HCl}$ . After the precipitate of  $\text{GeS}_2$  had coagulated, it was filtered and washed with 6 N  $\text{HCl}$  saturated with  $\text{H}_2\text{S}$ . The filter with the precipitate on it was dried and ignited. After the carbonaceous matter had been driven off, conc.  $\text{HNO}_3$  was added to insure complete conversion of  $\text{GeS}_2$  to  $\text{GeO}_2$ . The residue was re-ignited and weighed as  $\text{GeO}_2$ . Results on 7 and 10 g. samples showed .15% and .18%  $\text{GeO}_2$ , which were considerably lower than the .25%  $\text{GeO}_2$  said by the New Jersey Zinc Co. to be present.

The loss of Ge can be laid to one or both of the following causes:

- (1) Incomplete precipitation, which was evidenced by further precipitation of  $\text{GeS}_2$  in the last filtrate after standing.
- (2) Loss of  $\text{GeS}_2$  by washing, because some colloidal  $\text{GeS}_2$  was observed to pass thru the filter on washing.

### Determination of Ge as $K_2GeF_6$ .

Like  $SiF_4$ ,  $GeF_4$  with KF produces a gray-green gelatinous precipitate of the formula  $K_2GeF_6$ . Altho this precipitate is slightly soluble in water (1 pt. in 180 pts.  $H_2O$  at  $18^\circ$ ) it was thot probable that the presence of alcohol would make the precipitation quantitative. However, the addition of 95% alcohol to an equal volume of saturated KF solution causes precipitation of KF and it is found necessary to use a 50% alcohol and water mixture to insure complete precipitation, and for washing.

10 g. of sample are distilled with 50 cc of 48% HBr in a 100 cc distilling flask. The distillate is collected in a 500 cc conical flask, containing about 10 cc of water into which the adapter dips. The mixture is distilled until the residue is nearly solid. The condenser and adapter are washed with a few cc of conc.  $HNO_3$  to dissolve any  $As_2S_3$  or  $GeS_2$  precipitated on the walls due to sulfide in the sample. To the distillate fuming  $HNO_3$  is added, 2 or 3 cc at a time, until the HBr is all converted to  $Br_2$ . The flask is cooled beneath a running tap, because the heat of reaction may volatilize some  $GeBr_4$  not yet oxidized. The liquid is first warmed

on a water-bath to volatilize the excess  $\text{Br}_2$  and then is heated over a flame until a precipitate of  $\text{GeO}_2$  begins to form. Before any  $\text{GeO}_2$  is allowed to settle and incrust on the sides of the vessel the solution is transferred to a Pt crucible and the evaporation to dryness completed over a water-bath. The white powdery residue of  $\text{GeO}_2$  and  $\text{As}_2\text{O}_5$  is dissolved in 2-3 cc of 48% HF and forms a clear slightly colored solution. To volatilize any impurity of Si, as  $\text{SiF}_4$ , the solution is evaporated to a few drops of a thick syrup. About 10 drops of HF are again added to dissolve the residue, after which 2cc of saturated KF solution is added. A gelatinous precipitate of  $\text{K}_2\text{GeF}_6$  is formed and is completely brought down by the addition of 2-3 cc of 50% alcohol. The precipitate is filtered off in a mat made of filter paper pulp in a Pt Gooch crucible. The residue is washed with 50% alcohol until free from K salts and dried at  $100^\circ$ - $150^\circ$  over a very low flame. The residue is weighed as  $\text{K}_2\text{GeF}_6$ . The results obtained are as follows:

Table II.

Wt. of Sample	Weight of $\text{K}_2\text{GeF}_6$	% $\text{GeO}_2$
10.3927 g	.0619 g	.235
10.3708	.0669	.254
10.0253	.0607	.239
10.8793	.0615	.223

The average of these results, .238%, agrees closely with the analysis of .25% given with the sample. The uniformity of the results indicate the quantitative nature of the separation, which is hereafter used as a standard method of analysis for Ge.

c). Methods of extraction of Ge.

According to Winkler, Ge metal is attacked by dry HCl gas, forming the volatile  $\text{GeCl}_4$ . The action of dry HCl gas on zinc was observed, because its use might prove to be a means of separation of metallic Ge from metallic Zn. Pure C.P. zinc was heated to  $150^\circ$  in a current of dry  $\text{H}_2$ , to reduce any film of oxide on the surface of the metal. The zinc was then cooled and weighed. Dry HCl gas was passed over the Zn at  $150^\circ$  and after 30-40 minutes the passage of HCl was discontinued and a stream of dry  $\text{CO}_2$  passed over the metal to cool it and to remove the remaining HCl gas. The residue was removed and weighed. About 2% of the Zn was found to have been attacked by the HCl gas.

Altho this procedure suggested a possible means of separation of Ge from Zn, it was not worked upon further, because in the present methods of Zn smel-

ting and purification, at no time is there the solid metal phase present. The heat losses involved in cooling the gaseous metal to a solid, and redistilling, are obviously too great to warrant further experimentation along that line of procedure.

#### Extraction of $\text{GeO}_2$ by hot $\text{H}_2\text{O}$ .

It was thought possible that, owing to the solubility of  $\text{GeO}_2$  in water (1 pt. in 95 pts.  $\text{H}_2\text{O}$  at  $100^\circ \text{C.}$ ),  $\text{GeO}_2$  might be extracted from the ore by leaching with hot  $\text{H}_2\text{O}$ . Small quantities of the sample were digested with hot or boiling water and filtered. On passing  $\text{H}_2\text{S}$  into the neutral filtrate, a yellow precipitate was obtained. Analysis showed this precipitate to be composed of  $\text{CdS}$  and showed the total absence of Ge. On acidifying the filtrate strongly with  $\text{HCl}$  and passing in  $\text{H}_2\text{S}$ , no precipitate was obtained, again showing total absence of Ge.

#### Extraction of Ge from solutions.

Because no method of separation of Ge from the sample either in the metallic state or by direct leaching proved practicable, it is evidently advisable to dissolve the sample first and separate the Ge in solution by (1) distillation of Ge as  $\text{GeCl}_4$ , or

(2) precipitation of Ge as  $\text{GeS}_2$  from a strongly acid solution of the sample and filtration.

Method I. In the distillation of the sample with  $\text{HCl}$ , not only  $\text{GeCl}_4$  distills over at the boiling temperature of the liquid in the distilling flask, but  $\text{AsCl}_3$  also. Therefore, the complete extraction of Ge involves not only a distillation, but also a separation from the As in the distillate. The separation of Ge from As can be accomplished by one of two ways: (1) Precipitation of both As and Ge as sulfides and treatment as on pages 7 and 8, or (2) By a method developed by Browning and Scott\*. In this procedure, 5-10 cc of a 10%  $\text{K}_2\text{CrO}_4$  solution, the amount depending upon the quantity of As present, is added to the sample in the distilling flask, followed by a few drops of conc.  $\text{H}_2\text{SO}_4$ . The mixture is then warmed for a few minutes to insure conversion of any As from  $\text{As}_2\text{O}_3$  to  $\text{H}_3\text{AsO}_4$ . 50-60 cc of 12 N  $\text{HCl}$  are added and the mixture distilled in a current of  $\text{CO}_2$  until about one-half of the solution has distilled over. The current of  $\text{CO}_2$  is continued until all free  $\text{Cl}_2$  is removed from the distillate, after which  $\text{H}_2\text{S}$  is passed in and a precipitate of  $\text{GeS}_2$  obtained. Browning and Scott claim a complete separation of Ge from As,

\*Am. Jour. Science 46, (1918) 663-5.

because the As is left in the residue as  $\text{H}_3\text{AsO}_4$  or nonvolatile  $\text{AsCl}_5$ . Actually, however, small traces of As were detected in the distillate, during the quantitative estimation of the Ge obtained by this procedure. The Ge is precipitated as  $\text{GeS}_2$  by  $\text{H}_2\text{S}$  in the distillate, filtered off and immediately dissolved in  $\text{NH}_4\text{OH}$ . The filter paper is washed with  $\text{H}_2\text{O}$  containing a little  $\text{NH}_3$  and the filtrate and washings evaporated to dryness. An ammoniacal solution of  $\text{GeS}_2$  decomposes on exposure to air with formation of  $\text{GeO}_2$ . When all free  $\text{NH}_3$  has been expelled, a yellow precipitate of  $\text{As}_2\text{S}_3$  separates. This is filtered off, washed and the filtrate and washings evaporated to dryness. The resulting residue of  $\text{GeO}_2$  is dissolved in  $\text{HF}$  and the Ge determined as  $\text{K}_2\text{GeF}_6$  in the manner previously described. Results obtained are as follows:

Table III.

Weight of Sample	Weight of $\text{K}_2\text{GeF}_6$	% $\text{GeO}_2$
13.7801 g	.0795 g	.244
11.9002	.0888	.294
12.3933	.0850	.270

The yields by this procedure are evidently quantitative. If used on a large scale, however, serious disadvantages present themselves.

A distillation, involving large quantities of corrosive substances like HCl and  $\text{Cl}_2$ , is expensive, because of the special materials needed for the apparatus, its deterioration and also because of the large amount of heat required. A method, which would avoid such a distillation, was next developed.

Method II. A 10 g. sample is dissolved in 50 cc conc. HCl and 100 cc  $\text{H}_2\text{O}$  and warmed to about  $80^\circ$ - $85^\circ$  to dissolve completely. On cooling, which is necessary in a subsequent treatment, a large amount of  $\text{PbCl}_2$  settles out and is filtered off.  $\text{H}_2\text{S}$  is passed into the filtrate and precipitates only Ge and As, because of the high H ion concentration.

The  $\text{GeS}_2$  and  $\text{As}_2\text{S}_3$  are filtered off and without washing are dissolved in  $\text{NH}_4\text{OH}$  and treated as on pages 7-8 or are dissolved in a minimum amount of  $\text{HNO}_3$ , 10-20 cc conc. HCl added and the solution distilled.

For application on a large scale, Method II was considered to be superior to Method I, for the following reasons:

(1) Method I involves a distillation of large volumes in order to separate Ge and As, whereas in Method II, the Ge and As are separated on a small scale, which avoids the expenditure of much heat.

(2) A distillation on a large scale involving the corroding action of HCl and of chlorine gas at 130° is avoided in Method II.

The most economical quantities of conc. HCl and of H<sub>2</sub>O to be used in the solution of a given amount of charge to be treated by Method II were worked out. Samples of equal weights of charge were each digested at room temperature with varying amounts of conc. HCl and H<sub>2</sub>O for 30-40 minutes, filtered, and the residue and filtrates each analyzed qualitatively. The residues were all dissolved slowly in hot water at 80° to 95° C. The results obtained are as follows:

Table IV.

cc 12N HCl used For 10 g charge	cc H <sub>2</sub> O used	Analysis of sulfids pptd. from filtrate by H <sub>2</sub> S	Analysis of residue
50	50	As, Ge, trace Pb	Pb, (trace Zn and Ge)
50	100	Pb, As, Ge	Pb, (trace Ge)
50	150	Pb, As, Ge	Pb
40	150	Pb, As, Ge, (small)	Pb
30	150	Pb, As	Pb

From the results in the above table it may be concluded that (1) if sufficient acid and H<sub>2</sub>O are used to once dissolve the charge, the residue is composed only

of  $\text{PbCl}_2$  ; (2) that for each gram of charge there must be at least 5 cc of 12 N  $\text{HCl}$  and 15 cc  $\text{H}_2\text{O}$  in order that the residue may consist only of  $\text{PbCl}_2$  and that  $\text{Ge}$  may be completely precipitated from the filtrate by  $\text{H}_2\text{S}$ .

Modification of Method II. It is evident that Method II still possesses several striking disadvantages, which are: (1) The use of  $\text{HCl}$ , which necessitates expensive special materials of construction; (2) the occurrence of  $\text{Pb}$  in each filtrate due to the moderate solubility of  $\text{PbCl}_2$  which makes the recovery of  $\text{Pb}$  difficult.  $\text{H}_2\text{SO}_4$  is then substituted for  $\text{HCl}$  in dissolving the charge. In this modified procedure, 10 g of charge are digested with 50 cc of 12 N  $\text{H}_2\text{SO}_4$  and 100 cc  $\text{H}_2\text{O}$  for about 30 minutes. A considerable rise of temperature (about  $40^\circ \text{C}$ ) takes place, which facilitates the filtration of  $\text{PbSO}_4$  from the solution. The filtrate is saturated with  $\text{H}_2\text{S}$  and a yellowish-white precipitate obtained, which coagulates quickly and filters readily. The filtrate does not give any more precipitate on again saturating with  $\text{H}_2\text{S}$ , and strongly acidifying with conc.  $\text{HCl}$ .

The substitution of  $\text{H}_2\text{SO}_4$  for  $\text{HCl}$  has the following advantages:

(1) All Pb and Sr are completely removed by  $H_2SO_4$ . No Pb is detectable in the solution after filtering off the  $PbSO_4$ . It is thus possible to completely recover the Pb as  $PbSO_4$  residue.

(2)  $H_2SO_4$  is a much less corrosive reagent than HCl. This fact makes possible the use of Cu or Pb materials of construction.

(3)  $H_2SO_4$  is a much cheaper reagent than HCl.

The disadvantage of using  $H_2SO_4$  is that a considerably greater temperature rise occurs than when HCl is used during the digestion of the charge with the acid and water mixture, because the solubility of the  $GeS_2$  increases with the temperature. Experiments were carried out, in which  $H_2S$  was passed at different temperatures into the solutions obtained by treating the sample with  $H_2SO_4$  and removing the  $PbSO_4$ . The results obtained are as follows:

Table V.

Temp. of soln.	Analysis of ppt. obtained.	Analysis of filtrate for Ge and As.
95°	As only	Ge only
80	As only	Ge only
65	As, Ge	Ge only
50	As, Ge	Ge and As absent

From the above results, two conclusions may be drawn. First, As and Ge may be completely separated by  $H_2S$  at 80-100°. Arsenic is completely precipitated

at such temperatures, whereas Ge is not at all. Second, that Ge can not be completely precipitated from acid solutions by  $\text{H}_2\text{S}$  at a temperature greater than  $50^\circ \text{C}$ .

Altho no Zn nor Ge was found in the  $\text{PbCl}_2$  residues obtained by treating a 10 g sample with 50 cc 12 N HCl and 100 cc  $\text{H}_2\text{O}$ , it was feared that due to the fact that Zn is present in large amounts and that  $\text{ZnSO}_4$  is less soluble in  $\text{H}_2\text{O}$  than  $\text{ZnCl}_2$ , the  $\text{PbSO}_4$  residue might contain appreciable amounts of  $\text{ZnSO}_4$ . Accordingly, the  $\text{PbSO}_4$  residue obtained by treating a 10 g sample with 50 cc 12 N  $\text{H}_2\text{SO}_4$  and 100 cc  $\text{H}_2\text{O}$  was washed a few times with  $\text{H}_2\text{O}$ , the residue sucked as dry as possible after each washing and finally dissolved in hot HCl, cooled, and the  $\text{PbCl}_2$  obtained filtered off. The filtrate was analyzed for Ge and Zn, which were found to be absent.

Acknowledgment is hereby made to Dr. A.A. Noyes for his proposal of the problem and for his many valuable suggestions.

#### V. Summary.

(1) A quantitative method of analysis was adapted for the determination of Ge as  $\text{K}_2\text{GeF}_6$ . Fairly concordant results gave percentage of  $\text{GeO}_2$  in sample as 0.24%.

(2) A method was worked out for the extraction of Ge by the distillation of the sample, but was abandoned because it was not suitable for large-scale work.

(3) A second method was developed for the extraction of Ge by dissolving the charge in  $\text{H}_2\text{SO}_4$ , decanting, and precipitating the Ge and As as sulfides by  $\text{H}_2\text{S}$  and filtering. The residue of  $\text{GeS}_2$  and  $\text{As}_2\text{S}_3$  could then be treated on a small scale to obtain pure  $\text{GeS}_2$ . By this method, nearly quantitative yields of a pure product were obtained.