UNITED STATES GEOLOGICAL SURVEY

TEI-267

# THE EFFECT OF ASHING TEMPERATURES ON THE VOLATILITY OF GERMANIUM IN LIGNITE SAMPLES

By
Wendell P. Tucker
Claude L. Waring

**This preliminary report is released without editorial and technical review for conformity with official standards and nomenclature, to make the information available to interested organizations and to stimulate the search for uranium deposits.**

September 1952



**Prepared by the Geological Survey for the**
**UNITED STATES ATOMIC ENERGY COMMISSION**
**Technical Information Service, Oak Ridge, Tennessee**

CHEMISTRY

In the interest of economy, this report has been reproduced direct from copy as submitted to the Technical Information Service.



AEC, Oak Ridge, Tenn.-W26677

CONTENTS



TABLES

# THE EFFECT OF ASHING TEMPERATURE ON THE VOLATILITY OF GERMANIUM IN LIGNITE SAMPLES *

by

Wendell P. Tucker

and

Claude L. Waring

## ABSTRACT

A study has been conducted to provide data on the loss of germanium from ashed lignite samples. The lignite samples, of known germanium content, were ashed at various temperatures as high as 1000 C with varying rates of heating and varying amounts of surface area of the lignites. The results indicate that no germanium was volatilized during the various ignitions.

## INTRODUCTION

The Geological Survey is currently investigating radioactive lignites on behalf of the Atomic Energy Commission. As part of this study many hundreds of samples of ashed lignites are being analyzed spectrographically by semiquantitative methods for a total of 69 elements. One of the elements of prime importance as a possible byproduct in any processes that may be developed to extract uranium from lignites is germanium.

The lignite samples are ashed at temperatures exceeding 500 C in preparation for spectrographic analysis. The question arises whether germanium is lost by volatilization during such ashing and therefore would not

---

*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

be detected (even if originally present) in the spectrographic analysis.

References 1,2/ in the literature caution the analyst about loss of germanium by volatilization if the ashing of samples of high organic content is conducted at temperatures exceeding 500 C. No data, however, have been presented to show a detectable loss of germanium when the samples were ashed at higher temperatures or at various rates of heating.

Tests were conducted in the Trace Elements Section Washington Laboratory on lignite samples to determine if any germanium is lost either when the samples are ashed at various temperatures as high as 1000 C or when the rate of heating and the surface area of the samples are varied.

The germanium compounds in lignite samples are uncertain. The halides, oxides, and sulfides of germanium are volatile when heated under special conditions. These compounds are very unstable, and it is unlikely that germanium, except as the halides, would remain in these unstable states in the presence of air and moisture long enough to volatilize in any appreciable amount. It is thought that the unstable germanium compounds would oxidize quickly to the stable dioxide under the conditions of the tests described in this report.

Insufficient sample prevented the establishment of the temperature at which the germanium does volatilize.

## THREE EXPERIMENTS

1. The purpose of this first experiment was to determine if germanium is lost by gradually heating the lignite samples. The test consisted of gradually heating the samples containing three percentage ranges of

---

1/ Ahrens, J. W., Spectrochemical analysis, p. 216, 1950.
2/ Goldschmidt, V. M., and Peters, C., Geochemistry of germanium, Gesell. Wiss. Gottingen, Math.-Phys. Kl 3, p. 141, 1933.

germanium to 1000 C with interruptions at various temperatures to determine the percent of germanium.

Samples weighing 1 g were placed in a muffle furnace at 25 C, the temperature gradually increased to 200 C and held for 4 hours. The samples were cooled, weighed, and a portion removed for spectrographic germanium determinations. A similar procedure was repeated at 300, 400, 500, 800, and 1000 C for sample 83e; and at 500, 800, and 1000 C for samples 83R and WyO. The spectrographic germanium determinations are shown in table 1. The figures were calculated on the basis of ash at 500 C. Gradual heating indicated no loss of germanium even at the final high temperature.

Table 1.--Spectrographic germanium results on lignite samples that had been heated gradually

| Sample no. | Ashing temp. (C) | Ashing time (hr) | Percent Ge in ash 1/ |
|---|---|---|---|
| 83 R | 200 | 4 | ---- 2/ |
| 83 R | 500 | 4 | 1.10 |
| 83 R | 800 | 4 | 1.12 |
| 83 R | 1000 | 2 | 1.12 |
| WyO | 200 | 4 | ---- 2/ |
| WyO | 500 | 4 | 0.010 |
| WyO | 800 | 4 | 0.013 |
| WyO | 1000 | 2 | 0.012 |
| 83e | 200 | 4 | ---- 2/ |
| 83e | 300 | 4 | 0.59 |
| 83e | 400 | 4 | 0.60 |
| 83e | 500 | 4 | 0.60 |
| 83e | 800 | 4 | 0.60 |
| 83e | 1000 | 2 | 0.55 |

1/ Calculated on the basis of ash at 500 C.

2/ No spectrographic germanium results obtained, due to high organic content remaining in the samples.

2. The purpose of this second test was to determine the germanium loss, if any, by rapid heating of the lignite samples.

An investigation of the routine ashing procedure was conducted. The procedure consisted of rapidly heating the lignite samples in porcelain crucibles over Bunsen burners for a period of 45 minutes, then transferring to a muffle furnace already at 800 C, and holding the samples at this temperature for 3 1/4 hours. The samples were cooled, weighed, and the germanium content determined spectrographically. The results are shown in table 2, as calculated on the basis of ash at 500 C. The data obtained by this test indicated no loss of germanium.

Table 2.--Results of spectrographic germanium determinations on lignite samples that had been heated rapidly

| Sample no. | Ashing temp. (C) | Ashing time (hr) | Percent Ge in ash 1/ |
|---|---|---|---|
| 83 R | 800 | 4 | 1.10 |
| WyO | 800 | 4 | 0.010 |
| 83 e | 800 | 4 | 0.059 |

1/ Calculated on the basis of ash at 500 C.

3. The purpose of the third experiment was to determine the germanium loss when ashing was accomplished by rapid heating of samples with a relatively large surface area and also of samples with small surface areas--the worst possible conditions.

If a large surface area of sample is exposed to air, it is to be expected that, even with rapid heating, any compounds of germanium would be rapidly oxidized to $GeO_2$ which is not volatile, and therefore no loss of germanium would occur. Accordingly 1-g samples were spread in thin layers in 260-ml platinum dishes and placed in the muffle furnace at

1000 C for a period of one hour. The results, calculated on the basis of ash at 500 C, are shown in table 3, and they indicate no loss of germanium under the above conditions.

To test any loss of germanium from samples heated under small-surface-area conditions, 3 to 5 g of the lignite samples were dried at 100 C, packed in J. L. Smith crucibles, and placed in a muffle furnace at 1000 C for one hour. A violent evolution of gases was observed which persisted for several minutes. The samples were then transferred to platinum dishes and heated for another hour at 1000 C. Spectrographic germanium determinations, calculated on the basis of ash at 500 C, are shown in table 4. The results indicated no loss of germanium under these experimental conditions.

Table 3.--Spectrographic germanium results obtained after lignite samples had been rapidly heated in wide platinum dishes

| Sample no. | Ashing temp. (C) | Ashing time (hr) | Percent Ge in ash 1/ |
|---|---|---|---|
| 83 R | 1000 | 1 | 1.13 |
| WyO | 1000 | 1 | 0.012 |
| 83 e | 1000 | 1 | 0.62 |

1/ Calculated on the basis of ash at 500 C.

Table 4.--Spectrographic germanium results obtained after lignite samples had been rapidly heated in J. L. Smith crucibles (small surface area)

| Sample no. | Ashing temp. (C) | Ashing time (hr) | Percent Ge in ash 1/ |
|---|---|---|---|
| 83 R | 1000 | 2 | 1.10 |
| WyO | 1000 | 2 | 0.012 |
| 83 e | 1000 | 2 | 0.61 |

1/ Calculated on the basis of ash at 500 C