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DETERMINATION OF GERMANIUM IN ORIGINAL, UP-GRADED KOTLI COAL AND ITS TAILINGS

Nisar Ahmad, S. Ali Husain and Inayat-ur-Rahman

Fuel Research Centre, PCSIR Laboratories, Off University Road, Karachi

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In a Kotli coal sample, with 30 % ash, germanium was found up to 8.1 μg/g. Coal was up-graded by the froth flotation technique using ethanolamino-oleate as a flotation agent. The up-graded sample with 13 % ash, contained germanium up to 6.6 μg/g. In the tailings, which contain 37 % ash germanium was found up to 11.4 μg/g. Thus extraction of germanium from tailings is considered more economical, as germanium was shown to be concentrated in the mineral matter.

Key words: Germanium, Coal, Tailings.

INTRODUCTION

The study was done to find out whether germanium is present in organic moities or as inorganic minerals in coal to help decide whether germanium extraction is techno-economically feasible from the tailings or up-graded coal. Kotli coal was selected for this purpose. Kotli is in Azad Kashmir where semi-anthracite coal is found. This coal contains high fixed carbon, low volatile matter, high sulphur and high mineral matter i.e. moisture 1.2 %, ash 30 %, V.M. 11.2 % total sulphur 5.3 %.

The mineral matter varies from place to place. The sample under study had 30 % ash while the up-graded product had 13 % and its tailings 37 % ash (dry basis). Kotli coal was up-graded by the froth flotation technique [1] and the correlation between ash percentage and the amount of germanium was studied in up-graded coal and its tailings. For the determination of germanium the colorimetric method was used. In colorimetery, generally, three methods namely phenylfluorone, oxidised hematoxylin and molybdenum blue methods are known. Determination of germanium was done by a colorimetric method using phenylfluorone which gives a very critical absorbance at 510 nm without interference of impurities such as silicon, phosphorus and arsenic which are commonly present in coal. For the phenylfluorone method pre-ashing is not used as it requires extreme precautions due to the high volatility of germanium under strong oxidising conditions [3]. Phenylfluorone is four times as sensitive as molybdenum blue [4]. Hence the spectrophotometric readings of the three coal samples (untreated, up-graded and its tailings) were noted at 510 nm using phenylfluorone as a complexing agent.

Sagar and Manfred distilled $GeCl_4$ with HCl and determined germanium spectroscopically using phenylfluorone in coals and ores [5]. Wang, Humigong, Gong and Guguan have determined germanium in rocks using both phenylfluorone and poly (vinylpyrolidone)-stilbazo. The germanium levels determined were 0.005 % and 0.0048 % respectively [6].

Preparation of calibration chart [7]. The spectrophotometer used in this study was a Bausch and Lomb spectronic-21 and the temperature was maintained at 20°. The wavelength used was 510 nm.

A calibration chart showing absorbance vs concentration was drawn for ascertaining molar absorbance to be used in the final calculation.

A stock solution (1 litre) of sodium germanate was prepared by fusing 1.4408 grams of germanium dioxide (Merck 99.99 % purity) with 5 grams of sodium carbonate (anhydrous) at 1000°, dissolving it in water and making the volume to one litre. Before making up the volume the pH was adjusted to 6.8 by adding HCl. The pH was measured by Kent pH – meter using standard buffer solution of pH 4–9. Freshly prepared 1 ml stock solution was used for the experiments. Aliquots of different concentrations of germanium solutions were prepared with distilled water for use. The absorbance was noted at 510 nm using a blank reference.

Table 1. Different concentrations of standard solutions used.

Solution No.	Working solution (ml)	Distilled water (ml)	Gum arabic (ml)	HCl conc. (ml)	Phenyl-fluorone (ml)	Concentration of Ge μg/g.
1.	0	20	5	5	15	Blank
2.	0.5	19.5	5	5	15	0.1
3.	1.0	19	5	5	15	0.2
4.	2.0	18	5	5	15	0.4
5.	4.0	16	5	5	15	0.8
6.	5.0	15	5	5	15	1.0

Table 2. Absorbance at 510 nm compared with blank.

Solution No.	Absorbance 1	2	3	Mean taken
2.	0.072	0.072	0.072	0.072
3.	0.171	0.171	0.171	0.171
4.	0.372	0.370	0.370	0.370
5.	0.734	0.734	0.734	0.734
6.	0.905	0.903	0.903	0.903

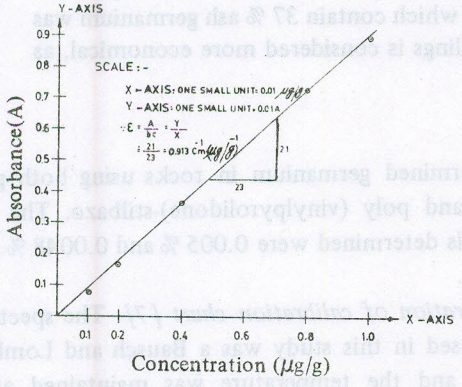

Fig. 1. The calibration chart drawn by plotting absorbance against concentration.

Molar absorbtivity (Σ) has been calculated as indicated in chart for application in the final formula.

$$A = bc$$

$$\text{i.e. } \Sigma \frac{A}{b}$$

Where A = Absorbance, b = Path length of the cell (1cm), c = Concentration (μg/g), Σ = Molar absorbtivity (0.913) (calculated from the chart).

Accuracy of the technique. In order to ascertain the accuracy of the phenylfluorone method, one ml of the prepared stock solution was diluted to 100 ml. One ml of diluted solution contains 0.01 mg of germanium equivalent to 0.001 %.

To one ml of the working solution, 24 ml distilled water and 25 ml concentrated HCl were added. Distillation was carried out as for unknown samples with condensation at a temperature below 20°, circulating ice-cold water through the condenser.

Twenty ml distillate was collected, as germanium tetrachloride distills over completely in this volume [8]. This distillate was divided into two equal parts. To each part 15 ml distilled water, 5 ml gum arabic solution and 15 ml phenylfluorone solution were added.

The solutions were made up to 50 ml with distilled water and absorbances noted at 510 nm, proving the accuracy of the method for the future determination of germanium in the unknown samples.

Absorbance	1	2	3	Mean taken
Portion 1	0.091	0.105	0.102	0.099
Portion 2	0.089	0.084	0.085	0.086

Germanium found =

$$C = \frac{(A_1 + A_2)\,50}{b\,\Sigma \times 1000}$$

$$= \frac{(0.099 + 0.086)50}{0.913 \times 1000}$$

$$= 0.01 \text{ mg/g}$$

$$= 0.001\ \%$$

Preparation of reagents. Phenylfluorone. Phenylfluorone (0.03 g) was dissolved in a mixture of 85 ml alcohol (85 %) and 5 ml sulphuric acid (1 + 6), diluted to 100 ml with alcohol after slight initial warming.

Gum arabic. Powdered gum arabic (1 g) was dissolved in 200 ml hot water and filtered.

EXPERIMENTAL

A mixture of Kotli coal (0.5 g; particle size-60 mesh BSS) and anhydrous sodium carbonate (0.5 g), and heated at 600° for three hours and then fused at 1000° for 15 minutes. This was then treated with 1 + 1 HCl (8 ml), and diluted to 30 ml. This was followed by a further addition of 25 ml concentrated HCl, in order to make a 6N solution. The germanium tetrachloride formed was distilled, circulating ice-cold water through condenser, keeping the temperature below 20°.

The germanium tetrachloride was completely recovered [8] in a 20 ml distillate. It contained 10 ml concentrated HCl. This was divided into two portion so that each portion contained 5 ml concentrated HCl and each was made up to 50 ml with gum arabic (5 ml), phenylfluorone solution (15 ml) and distilled water.

This solution was maintained at 20° for 30-60 minutes for the development of colour [9] before absorbance was noted. This experiment was repeated with the up-graded Kotli coal and its tailings.

Absorbances noted for the three samples were as under:

1. Kotli coal sample (untreated).

Absorbance	1	2	3	4	Taken
Portion 1	0.038	0.040	0.040	0.040	0.040
Portion 2	0.040	0.040	0.040	0.040	0.040

Weight of the sample = 0.5404 g
Germanium found 8.1 μg/g

2. Kotli coal sample (up-graded).

Absorbance	1	2	3	4	Taken
Portion 1	0.033	0.036	0.033	0.033	0.033
Portion 2	0.032	0.033	0.033	0.033	0.033

Weight of the sample = 0.5502 g
Germanium found = 6.6 μg/g

3. Kotli coal sample (tailings).

Absorbance	1	2	3	4	Taken
Portion 1	0.058	0.058	0.059	0.058	0.058
Portion 2	0.061	0.062	0.061	0.061	0.061

Weight of the sample = 0.5725 g.
Germanium found = 11.4 μg/g.

Results at a glance.

No.	Sample	Ash % (d-basis)	Germanium μg/g
1.	Kotli coal (original)	30%	8.1
2.	Kotli coal (up-graded)	13%	6.6
3.	Kotli coal (tailings)	37%	11.4

CONCLUSION

The original Kotli coal sample with 30 % ash contained 8.1 μg/g germanium while the up-graded sample had 6.6 μg/g germanium. It is quite evident from the results that the mineral matter has a direct relationship to the amount of germanium present i.e. greater the mineral matter, greater the amount of germanium in coal. This is further confirmed by the experimental results that the tailings of this up-graded coal with an ash percentage of 37 % contained 11.4 μg/g. germanium. On the basis of these findings it can be concluded that germanium extraction from the tailings is economically more feasible.

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