Online Resource 4 – Germanium enrichment during the processing of thermal coals

Accompanying the article: On the geological availability of germanium

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**Introduction**

The main purpose of this document is to provide the interested reader with additional information on the detailed reasoning which led to the three processing scenarios and the corresponding cut-off grades used in our calculations. It also contains a short evaluation of the ash-problem referred to in the main text.

From the main article, it will be remembered that a cut-off grade of 0.1 wt.% Ge for the fly-ash of thermoelectric power-stations was chosen for our calculations since this value was commonly applied in the past (Howes and Lees 1955, Yudovich and Ketris 2003), and since it is not expected that modern technological advances will have led to an increase in the minimum treatable concentrations.

**Germanium enrichment in coal ashes and the ash-problem**

To estimate the concentrations in coal necessary to produce ashes with certain minimum Ge concentrations, the overall enrichment occurring during the various stages of coal processing and combustion needs to be quantified. The concentration of germanium in the final ash product is given by:

\[
c_{\text{ash}}(\text{Ge}) = c_{\text{coal}}(\text{Ge}) \times \prod_i x_i \quad (\text{eqn.OR.4.1})
\]

where \(c_{\text{coal}}(\text{Ge})\) denotes the germanium concentration of the raw coal, \(A_d^{\text{coal}}\) denotes its ash content as a proportion of weight, and the \(x_i\) are factors describing the various enrichment processes. Given the minimum required \(c_{\text{ash}}(\text{Ge})\), as well as \(A_d^{\text{coal}}\) and all the relevant \(x_i\), the minimum required \(c_{\text{coal}}(\text{Ge})\) can be calculated by rearranging (eqn.OR.4.1) as follows:

\[
c_{\text{coal}}(\text{Ge}) = \frac{c_{\text{ash}}(\text{Ge}) \times A_d^{\text{coal}}}{\prod_i x_i} \quad (\text{eqn.OR.4.2})
\]

It can be seen from this equation that \(c_{\text{coal}}(\text{Ge})\) is, to a first approximation, expected to be linearly dependent on \(A_d^{\text{coal}}\). This is what leads to the ash-problem because such a dependence greatly complicates calculations. Namely, it would necessitate separate calculations, using separate sets of cut-off grades, for coals with different ash contents. Fortunately, such a treatment would still be possible without actually splitting our datasets since Ge concentrations and ash contents are statistically independent. Nevertheless, such a complication is highly undesirable and could only be avoided if one or more of the \(x_i\) are also linearly dependent on \(A_d^{\text{coal}}\). This possibility will be given detailed consideration below.
Enrichment processes

Two main processes may lead to an enrichment of germanium in the final ash product: 1) washing of coal to remove mineral ash, and 2) volatilisation and subsequent condensation onto fly-ash particles of germanium compounds during combustion:

1) Washing of coal: There are two main contributors to the washing enrichment factor, $x_1$: a) the affinity of Ge for organic matter and its concomitant enrichment in the low-density fractions of coal, and b) the often significant reduction in ash content of the washed coal. Unfortunately, detailed quantitative data on this problem is rather limited as illustrated by the comprehensive collection of literature data provided in Table OR.4.1. From this, it can be seen clearly that the reduction in ash content contributes much more to $x_1$ than the increased Ge concentrations in the low-density fractions. A plot of that data for which Ge-recovery in the light coal fraction was on the order of 30% of total Ge is given in Fig. OR.4.1a. This shows that $x_1$ is strongly dependent on $A_{d_{coa}}$. A regression line to the data is given, but it should be emphasised that such a relationship is approximate and only expected to hold for ash contents larger than about 5 – 7 wt.%, below which total enrichment should level off. This regression nevertheless gives a first way of estimating $x_1$ for different values of $A_{d_{coa}}$.

More data is available, however, on the reduction of the ash content of the float fraction alone (Zubovic et al. 1961). This data is plotted in Fig. OR.4.1b along with the data from Fig. OR.4.1a. The plot clearly shows the dependence of the ash reduction factor on the initial ash content of the coal. It will be noted that, although there is quite a large amount of scatter, the regression line comes reasonably close to $y = (1/6)A_{d_{coa}}$ which would be the relationship expected for a reduction of the ash content to a base level of 6 wt.%. Since the affinity of Ge to the low-density fractions might be assumed to be independent of $A_{d_{coa}}$ for the typical range of ash contents (< 50 wt.%), it is fair to base a second estimate of $x_1$ on the product of the ash reduction factor (calculated from the regression line in Fig. OR.4.1b) with the average enrichment of Ge in the low-density coal fractions. From the data in Table OR.4.1 (for which Ge recovery is about 30%), the average enrichment in the low-density fraction is about 1.5.

It remains to consider the effect of the linear dependence of $x_1$ on $A_{d_{coa}}$ on the calculation of cut-off grades for coal from (eqn.OR.4.2). Except for a small residual contribution, the effect of its increase with $A_{d_{coa}}$ should be cancelled by dividing through $A_{d_{coa}}$ such that a calculation of the cut-off grades of coal for just one value of $A_{d_{coa}}$ should be entirely sufficient for all our estimates concerning processing scenarious in which the coal is washed prior to combustion. Since washing also results in a much more uniform ash contents of the feed coal, the dependence of later enrichment processes on ash content may also be ignored.

The average ash contents of coals in our dataset are $20 \pm 2$ wt.% for brown coals and $19 \pm 1$ wt.%
for hard coals (where the errors given correspond to two times the standard error on the mean). Using the two methods of estimation described above we find $x_1 = 7.9$ and $x_1' = 5.4$ for an initial ash content of 20 wt.%, such that $x_1 \sim 6$ appears to be a good choice for all following calculations.

**Table OR.4.1 – Enrichment of Ge in low-density coal fractions**

<table>
<thead>
<tr>
<th>Enrichment factor</th>
<th>Percentage of total Ge</th>
<th>Density fraction (g/cm$^3$)</th>
<th>Ge$_{coal}$ (ppm)</th>
<th>Ge$_{one}$ (ppm)</th>
<th>Ash$_{coal}$ (%)</th>
<th>Ash$_{one}$ (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.6</td>
<td>30.2</td>
<td>1.3 – 1.4</td>
<td>1.5</td>
<td>5.6</td>
<td>26.9</td>
<td>7.2</td>
<td>Querol et al., 1995</td>
</tr>
<tr>
<td>3.6</td>
<td>55.3</td>
<td>1.3 – 1.5</td>
<td>1.5</td>
<td>2.0</td>
<td>26.9</td>
<td>9.7</td>
<td>Querol et al., 1995</td>
</tr>
<tr>
<td>6.7</td>
<td>45.1</td>
<td>&lt;1.25</td>
<td>12.0</td>
<td>15.0</td>
<td>20.4</td>
<td>3.8</td>
<td>Ruch et al., 1974</td>
</tr>
<tr>
<td>6.4</td>
<td>69.8</td>
<td>&lt;1.29</td>
<td>12.0</td>
<td>15.7</td>
<td>20.4</td>
<td>4.2</td>
<td>Ruch et al., 1974</td>
</tr>
<tr>
<td>5.4</td>
<td>32.3</td>
<td>&lt;1.29</td>
<td>6.0</td>
<td>10.0</td>
<td>15.7</td>
<td>4.8</td>
<td>Ruch et al., 1974</td>
</tr>
<tr>
<td>4.9</td>
<td>33.2</td>
<td>&lt;1.28</td>
<td>7.0</td>
<td>9.0</td>
<td>13.7</td>
<td>3.6</td>
<td>Ruch et al., 1974</td>
</tr>
<tr>
<td>4.1</td>
<td>61.2</td>
<td>&lt;1.32</td>
<td>7.0</td>
<td>9.4</td>
<td>13.7</td>
<td>4.5</td>
<td>Ruch et al., 1974</td>
</tr>
<tr>
<td>4.3</td>
<td>33.2</td>
<td>&lt;1.25</td>
<td>25.5</td>
<td>30.0</td>
<td>13.1</td>
<td>3.6</td>
<td>Ruch et al., 1974</td>
</tr>
<tr>
<td>3.3</td>
<td>61.9</td>
<td>&lt;1.26</td>
<td>25.5</td>
<td>30.5</td>
<td>13.1</td>
<td>4.8</td>
<td>Ruch et al., 1974</td>
</tr>
<tr>
<td>2.0 – 2.5</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Stadnichenko et al., 1953</td>
</tr>
<tr>
<td>1.3</td>
<td>N/A</td>
<td>&lt;1.55</td>
<td>19.1</td>
<td>20.1</td>
<td>9.59</td>
<td>7.6</td>
<td>Mastalerz et al., 2004</td>
</tr>
<tr>
<td>1.1</td>
<td>N/A</td>
<td>&lt;1.55</td>
<td>1.1</td>
<td>1.5</td>
<td>12.9</td>
<td>8.5</td>
<td>Mastalerz et al., 2004</td>
</tr>
</tbody>
</table>

**Fig. OR.4.1:** Enrichment of germanium in low-density coal fractions as a function of the ash content of the raw coal: a) total Ge enrichment vs. ash content – the red data-point represents a theoretical coal with 5 wt.% ash (see discussion in text), b) ash reduction factor (equal to the raw ash content divided by the ash content of the floated coal fraction) vs. raw ash content. Note that the regression line lies very close to the theoretical relationship for a base level of about 6 wt.% ash in the float fraction (i.e. $f(x) = 0.167x$).
2) **Volatileisation and condensation onto fly-ash particles**: The fly-ash enrichment factor, $x_2$, depends on many different variables describing the combustion process such as firing-type, combustion temperature, boiler symmetry, gas flow rate, ash content of the feed coal etc. (Yudovich and Ketris 2003). The most important one of these, however, primarily dependent on firing-type, appears to be the coefficient of slag removal (CSR) of the furnace. This relationship is clearly illustrated by the data provided in Table OR.4.2 showing higher $x_2$ for furnace-types with a high CSR. The CSR is equal to the proportion of ash leaving the furnace as bottom ash or slag, and varies greatly between different types of furnaces.

In the past, power stations mostly utilised lumpy coal feeds which were fired in fuel-bed furnaces (either moving grate or stoker fired), whereas today, virtually all power stations use pulverised coal combustion (PCC) due to the higher efficiency and throughput this firing-type is capable of achieving. Different types of PCC furnaces exist. They are divided into two groups: dry-bottom and wet-bottom furnaces, depending on whether the bottom ash leaves the furnace in solid or liquid form. The CSRs for these different types of furnaces are (Babcock and Wilcox Co. 1978):

- fuel-bed furnaces (both moving grate and stoker fired types) …..CSR $\sim 0.85$
- cyclone furnaces (PCC, wet-bottom)………………………………………0.70 $<\text{CSR} < 0.85$
- slag-tap furnaces (PCC, wet-bottom)……………………………………..CSR $<0.50$
- dry-bottom furnaces (PCC, dry-bottom)……………………………………..CSR $\sim 0.20$

Clearly, the now outdated fuel-bed furnaces would have been the most promising for the production of Ge-rich fly-ashes, as also indicated by the data in Table OR.4.2. But since all of the above PCC furnace-types are currently in use, it is reasonable to assume that coal with commercial Ge concentrations could be fired in dedicated cyclone furnaces (the most promising type) fine-tuned to produce the highest possible $x_2$ and germanium recovery. Therefore, it appears sensible to choose a value for $x_2$ reflecting optimum conditions. From Table OR.4.2 we see, that enrichment by a factor of 4 should easily be possible, at a total recovery rate of $>40\%$ of the original Ge content of the coal. We therefore take $x_2 = 4$.

**Processing scenarios and cut-off grades**

With the above enrichment factors, cut-off grades for three different (hypothetical) processing scenarios can be calculated. This subdivision is justified, since the losses incurred during the pre-enrichment processes might be significant (see above) and different processing routes should therefore be taken for coals in different concentration ranges, in order to minimise such losses.
Table OR.4.2 – enrichment of Ge in small size fractions of fly ash from power stations

<table>
<thead>
<tr>
<th>Enrichment factor</th>
<th>Percentage of total Ge</th>
<th>Size range of particles</th>
<th>Ge_{fly-ash} (ppm)</th>
<th>Ge_{raw-ash} (ppm)</th>
<th>CSR (%)</th>
<th>Boiler type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>33 to 65</td>
<td>43.0</td>
<td>&lt; 5 μm</td>
<td>7500</td>
<td>115 to 230</td>
<td>(85)</td>
<td>Grate-fired</td>
<td>Howes and Lees, 1955</td>
</tr>
<tr>
<td>18 to 37</td>
<td>42.5</td>
<td>&lt; 5 μm</td>
<td>3300</td>
<td>90 to 180</td>
<td>(85)</td>
<td>Retort-stoker fired</td>
<td>Howes and Lees, 1955</td>
</tr>
<tr>
<td>6.1</td>
<td>12.9</td>
<td>ESP – last two rows</td>
<td>139</td>
<td>22.7</td>
<td>72.7</td>
<td>PCC (Cyclone)</td>
<td>Mardon &amp; Hower, 2004</td>
</tr>
<tr>
<td>4.4</td>
<td>48.2</td>
<td>ESP – all three rows</td>
<td>101</td>
<td>22.7</td>
<td>72.7</td>
<td>PCC (Cyclone)</td>
<td>Mardon &amp; Hower, 2004</td>
</tr>
<tr>
<td>3.4</td>
<td>10.3</td>
<td>&lt;2.5 μm</td>
<td>19.6</td>
<td>5.7</td>
<td>34.6</td>
<td>PCC (Slag-tap)</td>
<td>Querol et al., 1995</td>
</tr>
<tr>
<td>2.4</td>
<td>32.5</td>
<td>&lt;10 μm</td>
<td>13.5</td>
<td>5.7</td>
<td>34.6</td>
<td>PCC (Slag-tap)</td>
<td>Querol et al., 1995</td>
</tr>
<tr>
<td>1.1/1.0</td>
<td>(80)</td>
<td>N/A (Baghouse filters)</td>
<td>208/21.9</td>
<td>193/21.2</td>
<td>(20)</td>
<td>PCC (Dry bttm.)*</td>
<td>Mastalerz et al., 2004</td>
</tr>
</tbody>
</table>

ESP – electrostatic precipitator
*Calculated assuming 5 to 10 % ash content in coal (washed bituminous coal from Hartley main seam and Northumberland soft coal) since only concentrations in the feed coal are given in the reference
^CSR from Babcock & Wilcox Co. (1978) for fuel-bed furnaces.
^No indication in paper. Assumed dry bottom boiler due to low enrichment in fly-ash (cf. Yudovich, Ketris (2003)). The firing type used in PCC power stations was inferred from the CSR calculated calculated from the data (cf. text).

First of all, the case in which the raw ash is used for Ge extraction is considered. This is effectively what is done with Russian and Chinese germanium-coals today. Taking $x_1 = 1$, $x_2 = 1$, $A^{*}_{\text{coal}} = 0.20$, and $c_{\text{ash}}(\text{Ge}) = 1000$ ppm, we find $c_{\text{coal}}(\text{Ge}) = 200$ ppm from (eqn.OR.4.2) as the minimum concentration in coal necessary for commercial extraction. Of course, the collection of all ash products for Ge extraction assumed in this and the following scenario does not necessarily make sense. In fact, it will always be sensible to collect only the bulk fly-ash and discard the bottom-ash. Depending on the type of furnace used, this fraction might be slightly or strongly enriched. If a dry-bottom furnace is used, then the concentration in the bulk fly-ash will be similar to that in the raw ash, however, due to the small CSR. Dry-bottom furnaces are the most widely used today, hence their use is the most likely. The use of other furnace types would reduce the required concentrations, since enrichment factors are generally higher, even in the bulk fly-ash and not just the finest fly-ash fractions (e.g. Mardon and Hower 2004). The ash-problem was ignored in this case, because it would have led to unnecessary complications in the calculations. Commonly, the cut-off grades for commercial high-Ge coals are on the order of 100 – 200 ppm (Seredin and Finkelman 2008) and this choice of cut-off grade therefore appears justified.

The second case corresponds to the extraction of Ge from the raw ash of coal, pre-enriched by...
washing. Taking $x_1 = 6$, $x_2 = 1$, $A^d_{coal} = 0.20$, and $c_{ash}(\text{Ge}) = 1000$ ppm, we find $c_{coal}(\text{Ge}) = 33$ ppm from (eqn. OR.4.2). For convenience we will use 32 ppm as our second cut-off grade. The total recovery of Ge in the concentrated ash product is expected to be about one third of the original amount, i.e. about 33%. Similar considerations as above apply concerning enrichment of the ash during combustion.

Finally, a scenario is considered where coals pre-enriched by washing are burnt in a dedicated cyclone furnace in a thermoelectric power station and only the fine fractions of the fly-ash are collected for germanium extraction. Taking $x_1 = 6$, $x_2 = 4$, $A^d_{coal} = 0.20$, and $c_{ash}(\text{Ge}) = 1000$ ppm, we find $c_{coal}(\text{Ge}) = 8$ ppm, with the total recovery of germanium in the concentrated ash product expected to be on the order of 13%.

It should be noted that these scenarios are not universal prescriptions for the treatment of all coals. Rather, empirical testing should precede the implementation of new processing steps or the restructuring of supply routes in any specific case, and the pathway producing the highest Ge yield at the lowest additional cost should be chosen. It is important to note in this context that the technologies which we considered for germanium enrichment are already in widespread use. Their implementation for the recovery of Ge-rich ashes is only a question of the restructuring of the current power production infrastructure to ensure that Ge-rich coals are processed separately, burnt in dedicated power stations or furnaces, and that fine fly-ash fractions are collected and sold to smelters.

It is furthermore worth noting, that Russian authorities classify thermal coals with Ge concentrations in excess of $\geq 5$ ppm as commercially viable for germanium extraction (Zharov et al. 1996), while in the Soviet Union, thermal coals with $\geq 10$ ppm Ge were classified as being of potential commercial interest (Kler 1988). That these values should be so close to the minimum value of 8 ppm calculated here is probably not a coincidence and lends additional credence to our estimates.

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