Calculation of qualitative and quantitative composition of Estonian oil shale and its combustion products. Part 1. Calculation on the basis of heating value

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Abstract

A method for calculation of the composition of Estonian oil shale and its combustion products is based on the various correlations governing the composition of this oil shale, and relations between its components. To understand better the properties of oil shale and the influence of mining conditions on oil shale quality, a general characterisation of Estonian oil shale is first presented. This unique fuel is utilized for power production, by direct firing in boilers. This paper presents calculations useful for the boiler design engineer for estimating the average characteristics of received oil shale as well as the possible deviations from these mean values.

The calculations in this part allow finding the composition of oil shale and the composition of combustion products of oil shale based only upon its heating value. Various considerations in performing oil shale combustion calculation are presented. A calculational example is presented in the appendix of this part. Part 2 of this study extends the method, given the availability of additional fuel analysis data.

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Keywords: Oil shale; Composition; Combustion products

1. Background

Oil shale, ranging in age from Cambrian to Tertiary, is located in many parts of the world. Deposits occupy thousands of square miles and contain many billions of barrels of potentially extractable shale oil. Total world resources of oil shale are conservatively estimated at 2.6 trillion barrels. By the late 1930s, the worldwide total yearly production of oil shale had risen to above 5 million metric tons. Production fell in the 1940s, during World War II. For the next 35 years it continued to rise, peaking in 1979–81 when in excess of 46 million metric tons of oil shale per year was mined, two-thirds of which was mined in the nation of Estonia. From the peak year of 1981, yearly production of oil shale declined to a low of about 15 million metric tons in 1999 due to downsizing of the Estonian oil shale industry (see for example John R. Dyni; http://www.emdaapg.org/Oil%20Shale.htm).

'Estonian Oil Shale' or 'Kukersite' was discovered in the North of Estonia more than 200 years ago. Chemical investigations carried out under the direction of Prof. C. Schmidt at Tartu (Dorpat) University proved the shale to be very rich in organic matter. The Estonian Government started the actual exploitation of oil shale in 1919 [1]. Investigations of oil shale for energetic use started at Tallinn Technical University (TTU) in the beginning of the 1920s. Characterizing the main qualities of Estonian oil shale and design of burning units and boilers for this fuel were the main objects of these investigations, but the commercial use of oil shale ash as a binding material was also investigated. The Department of Thermal Engineering (DTE) of TTU and its applications laboratory (founded in 1960) has investigated the properties of both oil shale as an energetic fuel and its ash. As result of these investigations, oil shale boilers utilizing pulverized firing (PF) technology were designed. Oil shale PF boilers have been used for tens of years in Estonian power plants (Balti—1390 MW and Eesti—1610 MW). Several boilers at the Balti power plant are now considered out-of-date, and no longer in regular service. Experience with these boilers showed that
<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A^d )</td>
<td>ash content in dry fuel (%)</td>
</tr>
<tr>
<td>( A^d_{\text{free}} )</td>
<td>sulphate-free ash (as % of dry fuel) formed during burning of fuel (%)</td>
</tr>
<tr>
<td>( A^r )</td>
<td>ash content in fuel, as received (%)</td>
</tr>
<tr>
<td>( A^r_{\text{boiler}} )</td>
<td>ash amount formed in boiler (per kg of as received fuel) (kg/kg)</td>
</tr>
<tr>
<td>( A^r_\Omega )</td>
<td>ash amount per MJ (per heating value of as received fuel) (kg/MJ)</td>
</tr>
<tr>
<td>( A^r_{\text{correc}} )</td>
<td>ash amount per MJ (per corrected heating value of as received fuel) (kg/MJ)</td>
</tr>
<tr>
<td>( (\text{CO}_2)^d )</td>
<td>carbonate CO2 content of dry fuel (%)</td>
</tr>
<tr>
<td>( (\text{CO}<em>2)^d</em>{\text{calc}} )</td>
<td>calculated carbonate CO2 content of dry fuel (%)</td>
</tr>
<tr>
<td>( (\text{CO}_2)^M )</td>
<td>carbonate CO2 content of as received fuel (%)</td>
</tr>
<tr>
<td>( \Delta (\text{CO}_2)^{d,M} )</td>
<td>correction factor for ((\text{CO}_2)^d) content (%)</td>
</tr>
<tr>
<td>( \text{FeS}_2 )</td>
<td>FeS2 content of sandy-clay part of oil shale (%)</td>
</tr>
<tr>
<td>( \text{FeS}<em>2</em>{\text{t-g}} )</td>
<td>assumed FeS2 content in sandy-clay part of oil shale (%)</td>
</tr>
<tr>
<td>( \text{FeS}<em>2^{d}</em>{\text{g}} )</td>
<td>marcasite content in dry fuel (%)</td>
</tr>
<tr>
<td>( \text{G}^d )</td>
<td>content of any component in dry fuel (%)</td>
</tr>
<tr>
<td>( \text{G}^c )</td>
<td>content of any component in carbonate part of oil shale (%)</td>
</tr>
<tr>
<td>( \text{G}^{c-c} )</td>
<td>content of any component in sandy-clay part of oil shale (%)</td>
</tr>
<tr>
<td>( \text{G}^o )</td>
<td>content of any component in organic part of oil shale (%)</td>
</tr>
<tr>
<td>( \text{gSO}_2 )</td>
<td>SO2 content in dry flue gas (mg/nm³)</td>
</tr>
<tr>
<td>( \text{G}_{\text{ash}} )</td>
<td>content of any component in ash (%)</td>
</tr>
<tr>
<td>( \text{k}_{\text{CO}_2} )</td>
<td>extent of carbonate decomposition</td>
</tr>
<tr>
<td>( \text{k}_{\text{CO}_2\text{-min}} )</td>
<td>minimum extent of carbonate decomposition</td>
</tr>
<tr>
<td>( \text{K}^d )</td>
<td>carbonate content in dry fuel (%)</td>
</tr>
<tr>
<td>( \text{K}^{\text{ash}} )</td>
<td>portion of carbonate carried over into ash (% of dry fuel) (%)</td>
</tr>
<tr>
<td>( \text{K}_{\text{s-c rec}} )</td>
<td>recalculation factor for sandy-clay fraction’s composition at other FeS2 content</td>
</tr>
<tr>
<td>( \text{k}_S )</td>
<td>extent of sulphur binding in the boiler</td>
</tr>
<tr>
<td>( \text{K}^{\text{dr}} )</td>
<td>recalculation factor from dry fuel to as received fuel</td>
</tr>
<tr>
<td>( \text{K}^{\text{ash-rec}} )</td>
<td>recalculation factor from sulphate-free ash to real composition</td>
</tr>
<tr>
<td>( \text{L}^d )</td>
<td>content of sandy-clay part in dry fuel (%)</td>
</tr>
<tr>
<td>( \text{L}^{\text{ash}} )</td>
<td>amount of sandy-clay part to be burnt to ash (as % of dry fuel) (%)</td>
</tr>
<tr>
<td>( \text{L}_{\text{ash}} )</td>
<td>ratio of sandy-clay part to be burnt to ash (%)</td>
</tr>
<tr>
<td>( \text{m}_{\text{w-s}} )</td>
<td>ratio of bomb water sulphur to total sulphur</td>
</tr>
<tr>
<td>( \text{Q}^d_\text{b} )</td>
<td>heating value of dry fuel in calorimetric bomb (MJ/kg)</td>
</tr>
<tr>
<td>( \text{Q}^d )</td>
<td>heating value of dry fuel (MJ/kg)</td>
</tr>
<tr>
<td>( \text{Q}^{\text{decomp carb}} )</td>
<td>decomposition heat of oil shale carbonates at full decomposition (MJ/kg CO2)</td>
</tr>
<tr>
<td>( Q^c )</td>
<td>lower heating value of oil shale’s organic part (MJ/kg)</td>
</tr>
<tr>
<td>( Q^S )</td>
<td>higher heating value of oil shale’s organic part (MJ/kg)</td>
</tr>
<tr>
<td>( Q^r )</td>
<td>heating value of as received fuel (MJ/kg)</td>
</tr>
<tr>
<td>( Q^{r\text{correc}} )</td>
<td>corrected heating value of as received fuel (MJ/kg)</td>
</tr>
<tr>
<td>( \Delta Q^r_{\text{carb}} )</td>
<td>correction factor for heating value due to incomplete decomposition of carbonates (MJ/kg)</td>
</tr>
<tr>
<td>( \Delta Q^r_{\text{sulph}} )</td>
<td>correction factor for heating value due to sulphur binding (MJ/kg)</td>
</tr>
<tr>
<td>( R^d )</td>
<td>organic part of dry fuel (%)</td>
</tr>
<tr>
<td>( S_0 )</td>
<td>content of organic sulphur in dry fuel (%)</td>
</tr>
<tr>
<td>( S_{0+p} )</td>
<td>content of organic and pyrite sulphur in dry fuel (%)</td>
</tr>
<tr>
<td>( S^d )</td>
<td>content of pyrite (marcasite) sulphur in dry fuel (%)</td>
</tr>
<tr>
<td>( S^d_{\text{sulph}} )</td>
<td>content of sulphate sulphur in dry fuel (%)</td>
</tr>
<tr>
<td>( S^d_{\text{t}} )</td>
<td>content of total sulphur in dry fuel (%)</td>
</tr>
<tr>
<td>( \text{SO}<em>2</em>{\text{ppm}} )</td>
<td>SO2 content in flue gases calculated as ppm (ppm)</td>
</tr>
<tr>
<td>( S^r_{\text{t}} )</td>
<td>total sulphur content in as received fuel (%)</td>
</tr>
<tr>
<td>( V_{\text{CO}_2} )</td>
<td>total CO2 amount in flue gases (nm³/kg)</td>
</tr>
<tr>
<td>( V_{\text{CO}_2\text{ carb}} )</td>
<td>CO2 amount formed by decomposition of carbonates (nm³/kg)</td>
</tr>
<tr>
<td>( V_{\text{CO}_2\text{ carbon}} )</td>
<td>CO2 amount formed by burning of carbon (nm³/kg)</td>
</tr>
<tr>
<td>( V^g )</td>
<td>total amount of flue gas (nm³/kg)</td>
</tr>
<tr>
<td>( V^Q_{\text{g}} )</td>
<td>amount of flue gas per MJ of as received fuel (nm³/kg)</td>
</tr>
<tr>
<td>( V_{\text{gQ correc}} )</td>
<td>amount of flue gas per MJ (per corrected heating value of as received fuel) (nm³/kg)</td>
</tr>
<tr>
<td>( V_{\text{H}_2\text{O}} )</td>
<td>amount of water vapour in flue gases (nm³/kg)</td>
</tr>
<tr>
<td>( V_{\text{d}_g} )</td>
<td>amount of dry flue gas (nm³/kg)</td>
</tr>
<tr>
<td>( V_{\text{N}_2} )</td>
<td>amount of nitrogen in flue gas (nm³/kg)</td>
</tr>
<tr>
<td>( V^o )</td>
<td>theoretical amount of air needed for burning (nm³/kg)</td>
</tr>
<tr>
<td>( V_{\text{O}_2} )</td>
<td>amount of oxygen in flue gas (nm³/kg)</td>
</tr>
<tr>
<td>( V_{\text{SO}_2} )</td>
<td>amount of SO2 formed by burning sulphur (nm³/kg)</td>
</tr>
<tr>
<td>( W^r )</td>
<td>total moisture of as received fuel (%)</td>
</tr>
<tr>
<td>( W^r_{\text{calc}} )</td>
<td>calculated moisture content of as received fuel (%)</td>
</tr>
<tr>
<td>( \Delta W )</td>
<td>correction factor for moisture content in fuel (%)</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>assumed excess-air coefficient in boiler, used for flue gas composition calculation</td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>standard excess-air coefficient, used for flue gas composition calculation</td>
</tr>
</tbody>
</table>
pulverized firing of Estonian oil shale is accompanied by a number of boiler operational problems-intensive fouling of heat transfer surfaces and intensive corrosion and wear of super heaters, due to aggressive components in fly ash. The main environmental emissions are of fine particles (fly ash) and sulphur dioxide.

The exhaust gas of the typical oil shale PF boiler consists of more than 1500 mg/nm³ of SO₂ in spite of the binding of ~80% of fuel sulphur by ash in the boiler. The average particulates content in flue gases was about 1500–2000 mg/nm³. Nowadays both power plants are equipped with new electrostatic precipitators and the particulates content in flue gases is under 100 mg/nm³.

Due to obsolescence of these power plants, as well as growing concerns about emissions, there is great interest in replacing the outmoded PF technology with more advanced combustion technology. Tests using atmospheric circulating FB conditions (CFB) with Estonian oil shale were performed in 1994 by Ahlstrom, later Foster Wheeler, Finland. In 1996 testing was done at Lurgi Lentjes Babcock (LLB) Germany in 1 MWth test facilities, and in the same year at ABB Combustion Engineering, in co-operation with University of British Columbia, Canada, at their laboratory FB test facility. The DTE of TTU was involved in these tests whose results have been previously reported [2].

The tests showed very low SO₂ emission levels, satisfying the most stringent emission limits in the world without the need for any additional flue gas desulphurisation equipment. Particulate emissions could be handled by installing bag filters or electrostatic precipitators and NOₓ is low thanks to the relatively low combustion temperatures. There is no doubt that current EC emission limits could be achieved.

As a result, it was decided that the Estonian oil shale power plants should be re-powered based on CFB technology. Foster Wheeler Energia OY (FW) will erect two units (4 × 215 MW CFB boilers) in 2003–2004. Re-powering of more energy units is foreseen in the near future. The design work accompanying installation of the new technology requires paying careful attention to the unique nature of oil shale fuels. Estonian oil shale differs in several ways from other energetic fuels. Boiler calculations used by boiler companies have not always taken into account these differences (e.g. the lime content in initial fuel). The calculation method presented in this work takes into account these differences and allows more precise calculation of results for oil shale fuels. The development of this calculational method was started simultaneously with the test firings in the CFB facilities and was used by Foster Wheeler while designing its new CFB oil shale boilers.

In designing oil shale boilers operating with new technology, it is important to correctly consider the properties of oil shale to be utilized, because the reliability and economy of boilers greatly depend on fuel properties. Again, Estonian oil shale is known as a problematic fuel and has caused great troubles in boiler operation. Possible changes in oil shale heating value in the future may also cause some changes in boiler operation conditions. It is necessary to consider all possible changes beforehand.

Optimal designs of boilers and their components may be conveniently found only when it is possible to predict the composition and properties of oil shale as a function of its heating value. The ability to predict is very important, because experimental measurements needed to estimate the composition and properties of oil shales of different heating values, as well as of their combustion products, are expensive and time-consuming. Their use for optimisation calculations is practically excluded, due to variability in the feeds. Similar considerations have led those who face fuel switching issues in coal-based power sector to develop generalized predictive methods, based on a minimum set of fuel characteristics.

Finding calculationally the composition of oil shale, and its combustion products, may be of interest in a case when, based upon the routine oil shale sample analysis data, knowledge of the general nature of that sample is needed, or predictions of boiler burning conditions are required.

Investigations have shown interrelations between oil shale heating value and composition as well as between characteristics estimated by technical analyses and composition. Based on these results, it is possible to determine from heating value and carbonate content information the composition of oil shale and its combustion products with sufficient accuracy for boiler calculations. Investigations have however, also shown that oil shales with the same heating values may differ somewhat in composition. Therefore, computational predictions should even be preferred to a single casual prediction made on the basis of a few sample analyses, insufficient for authentic statistical calculations.

The average component composition data for Estonian oil shale (given later in Table 2) are taken as the basis for calculations. Consequently, the calculation results (contents and amounts of different components) correspond to these initial average oil shale data. Some overall data about oil shale composition and properties are first presented as background for readers not familiar with oil shale in general and Estonian oil shale in particular.

### 2. Composition and properties of oil shale used in Estonian power plants

#### 2.1. Characterization of the Estonian oil shale basin

Examination of issues connected with composition and properties of oil shale as a fuel should be started using a stratigraphic characterisation of the Estonian oil shale basin. The oil shale bed is not homogenous, but has a complicated structure and consists of oil-shale layers of different quality that lie alternately with limestone interlayers. The bed thickness is maximal in the Jõhvi–Kohtla-Järve area. To
the west, south and east the thickness of the oil shale layers (as well as thickness of the entire bed) decrease. The total thickness of the payable bed in the Estonian field is 2.5–3.2 m, of which oil shale layers account for 1.8–2.6 m and limestone layers 0.6–0.7 m. The payable oil shale layers in the Estonian field are to the east of Kadrina, extending to the Narva River. Further to the east the total thickness of oil shale bed in the Leningrad field is 1.6–1.9 m in which 1.0–1.3 is oil shale. On the northern coast of Estonia the oil shale layers outcrop onto the earth’s surface. To the south, in the direction of Peipsi Lake, the depth of bed increases by 3.5 m/km [3–6].

Fig. 1 shows the general profile of the Estonian oil shale field. In Fig. 1 capital letters mark the oil shale layers beginning with the lowest layer. The payable layers are A–F. (To the east, in the Leningrad field, the number of payable layers decreases to only 4.) The structure of the oil shale bed of the Estonian field is exemplified by that the vicinity of the closed mine Käva 2, which is approximately in the central part of field between Kohtla-Järve and Jõhvi. This structure is what is presented in Fig. 1. The total thickness of that bed (including layers G and H) is ~5 m [4].

Table 1 characterizes the different layers. It should be noted that data about the various oil shale layers presented in the bibliography [3–7] by different authors are to some extent differing. That may be a result of observing the bed at different places, and is a common problem in characterizing geological resources.

Table 1 indicates that oil shale layers G and H, separated from lower ones by a meter-thick limestone layer are not used for production, mainly for economic reasons. The thin oil shale layers deeper than layer A also are not used. In the case of underground mining layer F forms the mine ceiling, but in the case of open pits, it is used.

### Table 1

<table>
<thead>
<tr>
<th>Layer</th>
<th>Average Thickness (m)</th>
<th>Heating value, ( q^d ) (MJ/kg)</th>
<th>Character of layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>~0.17</td>
<td>15.1</td>
<td>Not used for production</td>
</tr>
<tr>
<td>G/H</td>
<td>~0.23</td>
<td></td>
<td>Tight limestone</td>
</tr>
<tr>
<td>G</td>
<td>~0.28</td>
<td>16.3</td>
<td>Not used for production</td>
</tr>
<tr>
<td>F/G</td>
<td>~1.1</td>
<td></td>
<td>A clay-rich limestone with clayey oil shale interlayers</td>
</tr>
<tr>
<td>F</td>
<td>0.91</td>
<td>7.5–10.0</td>
<td>Contains plenty of intermediate oil shale interlayers of variable thickness.</td>
</tr>
<tr>
<td>E/F</td>
<td></td>
<td></td>
<td>In the oil shale base layer there are two [3,5,6] or three [2] layers of different heating value</td>
</tr>
<tr>
<td>E</td>
<td>0.39</td>
<td>15.1</td>
<td>A thin organic rich interlayer without fixed borders</td>
</tr>
<tr>
<td>D/E</td>
<td>0.13</td>
<td>2.9</td>
<td>The most important payable layer besides layer B. Limestone content is lower than in other layers</td>
</tr>
<tr>
<td>D</td>
<td>0.13</td>
<td>13.4</td>
<td>A thin organic rich limestone layer</td>
</tr>
<tr>
<td>C/D</td>
<td>0.24</td>
<td>0.6</td>
<td>Contains plenty of thin limestone layers, only with difficulty separable from upper and lower limestone interlayers</td>
</tr>
<tr>
<td>C</td>
<td>0.31</td>
<td>10.6</td>
<td>Limestone-rich layer</td>
</tr>
<tr>
<td>B/C</td>
<td>0.10</td>
<td>2.9</td>
<td>Layer of variable thickness containing organic matter in substantial amount</td>
</tr>
<tr>
<td>B</td>
<td>0.61</td>
<td>16.8</td>
<td>The most important payable layer containing small layers of crystal limestone</td>
</tr>
<tr>
<td>A/B</td>
<td>0.13</td>
<td>1.3</td>
<td>Interlayer A/B—the clayey limestone</td>
</tr>
<tr>
<td>A(_u)</td>
<td>0.07</td>
<td>10.4</td>
<td>The layer A, distributed into upper and lower zones. The upper one is a limestone-rich oil shale layer</td>
</tr>
<tr>
<td>A(_l)</td>
<td>0.04</td>
<td>2.9</td>
<td>A clayey organic-rich limestone layer</td>
</tr>
<tr>
<td>A(_l)</td>
<td>0.19</td>
<td>17.3</td>
<td>A clayey oil shale layer without limestone inclusions</td>
</tr>
</tbody>
</table>
2.2. Chemical-mineralogical composition of Estonian oil shale

Besides organic matter, Estonian oil shale consists mainly of limestone and clay, as Table 1 shows. The clay does not exist in the oil shale bed as a separate layer but is distributed into oil shale and limestone layers as a fine-grain addition, consisting of sand and clay. As shown in earlier investigations [8,9] the dry matter of oil shale consists of three separate components. These main components are:

1. The organic part
2. The sandy-clay part (including FeS2)
3. The carbonate part.

The total of these components in the dry matter of oil shale is 100%, meaning that there are no other significant mineral or organic components. The results of the previously noted investigations also established that the average composition of the main components is quite constant throughout. Hence, the composition of an oil shale sample is determined by the relative amounts of these three components in the sample. Data on the chemical and mineralogical composition of the separate main components of oil shale are based upon Refs. [8,9].

As shown by later investigations of the DTE/TTU, based on the results of later analyses of fuel actually used at power plants, the data of Refs. [7–9], needed some corrections concerning the fuel’s mineral part. (The organic part of oil shale was not investigated). The data on the chemical composition of oil shale’s main components and the observed range of oil shale mineral components’ contents derived from this more complete data set [7,11] are presented in Table 2.

The data presented in Table 2 were selected for developing versions of the calculation method, described below. The main mineralogical constituents of the carbonate part of oil shale are calcite and dolomite (~99.7%). The content of siderite is very low (~0.3%). The main minerals in the sandy-clay part are quartz (~23%), orthoclase (~28%), hydromuscovite (~23%) and marcasite (~9%). In addition to these, the sandy-clay part contains albite, anortite, limonite and others with total content less than 15%.

2.3. Characterisation of fuel used in the Estonian power plants

As was noted, the thickness of different layers changes when moving away from the central part of the oil shale field. Also, due to the stratified structure of the oil shale bed, the composition and properties of the fuel transported to any power plant depends to a great extent on mining and enrichment conditions. The latter determines the amount of limestone-rich interlayers included in commercial oil shale, which also determines the heating value and composition of the fuel. Properties of the fuel used in Estonian power plants have changed over time. There has been a pattern of decreasing oil shale heating value and increasing ash and CO2 content with time. The change in oil shale heating value used in the Estonian Power Pants, during years 1959–2001, is shown in Fig. 2.

At the present time the average lower heating value of oil shale (as received fuel) in large Estonian power plants is 8.3–8.4 MJ/kg, ash content A’ = 46% and CO2 content (CO2)M = 17–18.5%. Based on the opinion of the ‘Eesti Põlevkivi’ mining concern [10], in the long-term oil shale heating value will continue fall with time and over the next decade it will fall to approximately 8.2 MJ/kg. Here it should be noted that heating value of oil shale provided to power plants is not actually directly determined by a choice of mined oil shale bed, but depends mainly on contracts between producer and consumer. (As mines may select which beds to use to achieve contracted values).

The heating value of un-enriched as-mined oil shale, so called ‘mountain massive’, is ~6.7–6.9 MJ/kg. This means that at the present time, removing of limestone enriches the oil shale used at power plants to the indicated extent. Which oil shale is suitable for use in power plants depends primarily on price considerations. As acceptable heating value decreases, the enrichment costs will decrease and the price per MJ of oil shale at the mine will decrease. At the same
time, transport costs and costs for fuel preparation and ash handling at the power plant will increase. Also the amount of CO₂ emission per kWh from power plants will increase to some extent. All these considerations, and the changes in costs connected with them, will in the future determine the heating value of the oil shale that is economically most suitable. Costs connected with the fuel should be considered during renovation of oil shale power plants, when determining fuel specifications for the new boilers.

2.4. Main relationships between oil shale composition and heating value

The existence of relationships between the content of separate constituents, their composition and heating value is a precondition for finding correlations between the latter and the oil shale composition. These relationships were investigated in DTE/TTU over many years [12–14]. On the basis of these investigations, quite reliable relationships have been established. Results of one investigation [13], based on oil shale from the Sirgala open pit, established the relationship between the ash content $A_d$, the carbonate content, expressed as CO₂ from complete carbonate decomposition $(CO_2)_{ad}$, fuel moisture content $W_r$ and heating value $Q_{di}$ over quite a large range of heating value $Q_{di}$ over quite a large range of heating value—$Q_{di} = 7.5 \text{ to } 14.5 \text{ MJ/kg}$.

Power plants are typically supplied with fuel from several different producers. As the data showed, the composition of the fuel is to some extent variable. Because of that, the relationships obtained from an examination of the long-term database (1959–2001) of the Estonian power plants were used in developing the calculation method. These relationships are presented in Figs. 3–5. These data were preferred to those obtained from the Sirgala oil shale, because they represent better the actual range of commercial operations. There is naturally a great deal of similarity between correlations presented in Ref. [13] and those in Figs. 3–5.

An increase of moisture content in oil shale of higher heating value (Fig. 5) is the result of a higher content of organic matter and lower content of carbonates, due to association of moisture with the organic fraction. On other hand, an increase in organic matter and decrease in carbonates increases heating value that more than offsets the decrease due to moisture increase. Moisture is related to heating value, but also to other factors that do not necessarily correlate with the latter, hence the data on moisture in Fig. 5 are somewhat scattered, and the relationship is simply taken to be linear.

3. Calculation of the composition of oil shale and its combustion products from heating value

This paper presents a basic calculational method, termed ‘Calculation 1’, designed to provide an understanding of how changes in oil shale heating value affect the operational conditions of the boiler as well as the composition and amount of combustion products. Also this version is useful if comparison is needed of combustion products’ composition and amount, using the same oil shale at different combustion conditions. The next part of this series will present calculations assuming further analysis data to be available.

3.1. Initial data needed for the calculations

3.1.1. Data related directly to the fuel

The lower heating value of the as received fuel $(Q_r^f)$ is taken as the basis for calculations. Considering the fact that
FeS$_2$ contained in the sandy-clay part does not spread evenly over the oil shale, in the calculation program there is the possibility for insertion of an expected content of FeS$_2$. The fluctuation of FeS$_2$ content in the sandy-clay part may be greater than $\pm 2\%$. That fact influences the calculated value of organic and sandy-clay fraction content of the fuel. If there are no actual data for FeS$_2$ content, then the average content (9.3%) from Table 2 should be used.

The carbonate CO$_2$ content in oil shale may fluctuate significantly even at a fixed heating value (see Fig. 4). In consideration of this fact, a fluctuation correction factor ($\Delta$CO$_2$)$_{\text{M}}$ is introduced. Based upon DTE/TTU investigations, the limits for this factor are $-2.0$ and $+2.0$. In most cases the deviation of CO$_2$ content is smaller.

The recommendations for correction factor are based on the average data from power stations (Figs. 3–5). The data for some fuel shipments may vary more than the limits given above. When defining the maximum capacity of ash removal and gas cleaning systems, usage of this correction factor is essential.

Calculation 1 is the basic calculation for combustion products composition and amounts. There is a possibility of correcting the moisture content. Calculation 3 of the next part of this series can provide this information. The general calculational flowsheet is shown below.

It begins with the measured lower heating value $Q'_r$, at the top left of the figure. Use of the correlation of Fig. 5 provides an estimate of moisture content, which can be
modified as needed or desired by a correction factor (ΔW, see part 2). This permits calculation of a dry basis lower heating value (Q_d) from which Fig. 3 permits obtaining the ash content estimate and Fig. 4 the carbonate CO₂ content, (CO₂)_M_calc. Again, the availability of independent carbonate content information or a decision to use a conservative estimate correction factor as mentioned above, allows this carbonate content to be revised.

Once these preliminary estimates are in hand, the calculation of oil shale main components can begin, as shown on the right hand portion of the flowchart. In addition to the dry basis heating value, Q_d, and carbonate CO₂ content, (CO₂)_M, just obtained, the calculation will assume the average FeS₂ content of 9.3% from Table 2 and a heating value of the organic fraction, Q_o, described below.

### 3.1.2. Data related to the boiler operating conditions

The first such datum is the extent of carbonates decomposition (ECD) in the boiler, k_CO₂. The value of ECD, expressed as a fraction of carbonate mineral which is decomposed, releasing CO₂, varies for Estonian oil shale. It is 1 for pulverized firing (PF), ~0.8 for circulating fluidised bed (CFB) boilers, ~0.3 for pressurized fluidised bed (PFB) boilers. In the case of PFB boilers, sulphur binding and decomposition of MgCO₃ causes the decomposition of carbonates. The value of ECD is found by preliminary calculations. The recommended extent of sulphur binding in the boiler (k_S) 0.75–0.8 for PF and ~0.999 for CFB boilers. The excess-air coefficient α, at which value the SO₂ content in flue gas was defined, must be known (the excess-air coefficient is calculated in the dry gas using the formula α = 21/[21 − O₂], in which O₂ represents the percentage oxygen in the flue gas). The excess-air coefficient α, at which value the flue gas composition and amounts are calculated, must also be known priori (Schemes 1 and 2).

---

**Scheme 1. Calculation of qualitative and quantitative composition of Estonian oil shale and its combustion products.**
3.2. Calculation of the main components of fuel

3.2.1. Determining carbonate CO$_2$-, moisture- and ash-content as initial data for the calculation

Calculation of the main components of oil shale and its combustion products is based on the carbonate CO$_2$ content of the dry fuel. It is possible to calculate content of other main components (organic-, sandy-clay- and carbonate-part) of the fuel knowing the carbonate CO$_2$ content. Again, the basis of the CO$_2$ content calculation is the formula in Fig. 4 which describes the mean content of (CO)M as a function of the heating value of dry fuel:

\[
\frac{\text{CO}_2}{\text{M}} = \frac{20.323}{Q_d^{\text{i}}} + 0.012 (Q_d^{\text{i}})^2
\]

Using the formula in Fig. 5 a preliminary mean moisture content for as received fuel, at given heating value, can be found and corrected as needed by:

\[
W^\text{i} = W^\text{i}_{\text{calc}} + \Delta W
\]

Using the corrected value of moisture content the lower heating value $Q^\text{d}_\text{L}$ can be found as usual. As modest changes in heating value are not associated with drastic changes in Estonian oil shale composition \[13\], the calculation procedure given below is useful even if the heating value data have to be extrapolated.

The probable limits for carbonate CO$_2$ content can be found by correcting the calculated value (CO)M by a correction factor $\Delta (\text{CO}_2)^\text{M}$

\[
(\text{CO}_2)^\text{M} = (\text{CO}_2)^\text{M}_{\text{calc}} + \Delta (\text{CO}_2)^\text{M}
\]

This is really performed as part of a sensitivity analysis, reflecting the fact that imperfect knowledge of this parameter can have a significant impact on results.

The ash content in dry fuel $A^\text{d}$ is calculated using the formula given in Fig. 3. In this calculation method the ash content of dry fuel is used only to evaluate the results of calculations. Although there are possible fluctuations of $A^\text{d}$ at a particular heating value, a correction factor is not used in this case.

3.2.2. Mass fraction of the organic part ($R^\text{d}$)

To find the content of the organic part, the following data are needed: the heating value of the oil shale’s organic part, the heat of dissociation of carbonates contained in the carbonate part of the oil shale and the amount of heat released by burning FeS$_2$ contained in the sandy-clay part. The heating value of oil shale dry solids equals the heat of combustion of the organic part $Q^\text{O}_\text{d}$, less the heat for complete dissociation of carbonates contained in the dry solids, plus the heat released by burning FeS$_2$ contained in the sandy-clay part.

3.2.2.1. Heating value of the organic part of oil shale.

Calculation of the heating value of the organic part of oil shale is based upon the composition of organic part (data in Table 2). There are several well-known formulas used to calculate the heating value of solid fuels from their composition (D. Mendelejev’s, P.L. Dulong’s, W. Steuer’s formulas). Generally these are so-called universal formulas, and the calculated heating value of a fuel may differ somewhat from its real value. In the present calculation method, the coefficients for oil shale presented in investigation \[14\] were taken as a basis. These coefficients were recalculated to a MJ/kg basis, where the element symbols represent the mass percentages in the organic fraction. The higher heating value of the oil shale organic part may be calculated from the formula:

\[
Q^\text{O}_\text{d} = 36.680 C + 1.0623 H - 0.1339 O + 0.0658 S \\
+ 0.0106 N - 0.0280 Cl
\]

The higher heating value of the organic part of oil shale is found to be $Q^\text{O}_\text{d} = 36.680$ MJ/kg by using the average chemical composition from Table 2 in the formula above. The lower heating value of the organic part of oil shale is,

CALCULATION PROCEDURE FOR OIL SHALE MAIN COMPONENTS

**INITIAL DATA**

\[ Q^\text{i}, Q^\text{i}_{\text{e}}, (\text{CO}_2)^\text{i}, \text{FeS}_2 \]

**CALCULATED CONTENTS OF ORGANIC, CARBONATE, SANDY-CLAY PARTS AND FeS$_2$**

\[ R^\text{i}_{\text{om}} = f(\alpha', (\text{CO}_2)^\text{i}_{\text{om}}, \text{S}^\text{i}_{\text{p}}, Q^\text{i}) \]

\[ K^\text{i}_{\text{om}} = f((\text{CO}_2)^\text{i}_{\text{om}}) \]

\[ L^\text{i}_{\text{om}} = f(R^\text{i}_{\text{om}}, K^\text{i}_{\text{om}}) \]

**IF**

Abs(FeS$_2$ - FeS$_{\text{om}}$) < 0.005

**No**

\[ S^\text{i}_{\text{p}, \text{om}} = S^\text{i}_{\text{p}} + dS \]

**Yes**

\[ R^\text{i} = R^\text{i}_{\text{om}} \]

\[ K^\text{i} = K^\text{i}_{\text{om}} \]

\[ L^\text{i} = L^\text{i}_{\text{om}} \]
3.2.2.2. The heat of carbonate dissociation and heat of combustion of FeS₂. For finding the heat of carbonate dissociation, the typical composition of carbonate part of oil shale (in Table 2) is taken as a basis, as opposed to simply using the heat of dissociation of CaCO₃. The CaO mole percent in CaO + MgO is 84, and MgO mole percent is 16. One mole of CaO or MgO binds one mole of CO₂ in the carbonate fraction—consequently, 84% of CO₂ bonds with CaO and 16% of CO₂ bonds with MgO. The heat of dissociation of FeCO₃ is not considered because of the low content of this mineral. The heat of dissociation for CaCO₃ is 4.1232 MJ/kg and for MgCO₃ is 2.6156 MJ/kg. In the case of complete dissociation, the heat of carbonate dissociation is:

\[
Q^d = Q^d_s - 0.21831H = 36.680 - 0.21831 \times 9.70
\]

\[
= 34.560 \text{ MJ/kg} \quad (5)
\]

These calculation results [14] have been compared to results obtained by other formulae, at the same composition of organic part of oil shale, and the difference is no greater than 7% (~2.47 MJ/kg).

3.2.2.3. Calculation formula for finding the content of the organic part. Taking as the basis the calculated heating value of organic part of oil shale; the heat of dissociation of carbonates and the heat of combustion of FeS₂ the lower heating value of dry fuel is as follows:

\[
Q^d = (Q^d_s R^d - 3.882(\text{CO}_2)_M^d + 13.297S^d_p)/100
\]

where

\[
R^d = (100Q^d_s + 3.882(\text{CO}_2)_M^d - 13.297S^d_p)/Q^d
\]

The thermal effects of other possible processes in the mineral part of the fuel are relatively small (especially in the case of low temperature firing in fluidised bed boilers), and these are not taken into account in the above formulas.

3.2.3. Mass fraction of carbonate part \((K^d)\)

Using the calculated carbonate CO₂ content \((\text{CO}_2)_M^d\) in oil shale, the actual carbonate mass content of the oil shale can be found:

\[
K^d = 100(\text{CO}_2)_M^d/45.1
\]

where 45.1 is the mean value of CO₂ in carbonate part (Table 2).

The above calculation of course simply reflects the fact that CaO and MgO accompany the CO₂ in the carbonate.

3.2.4. Mass percentage of sandy-clay part \((L^d)\)

The mass percentage of the sandy-clay part is found by difference:

\[
L^d = 100 - R^d - K^d
\]

3.2.5. Calculation procedure

The contents of some constituents are dependent on others. A change in content of one constituent causes a change in content of another constituent. Because of this, the whole calculation of the contents of the main constituents is carried out in an iterative calculation as shown on the right hand part of the flow sheet above. To calculate the contents of the main constituents of oil shale a separate calculation program has been prepared. This program was written as a macro and works with the main program written in MS Excel. The content of pyrite sulphur \((S^d_p)\) is taken as the iteration variable, starting with an arbitrary value. The reason that this iteration is necessary, is that the initial assumption regarding pyrite sulphur has significant uncertainty associated with it. Pyrite can be found in both the sandy-clay and organic parts of the oil shale. On the basis of the iteration value of \(S^d_p\) in each cycle of calculation, the content of such components as \(R^d\), \(K^d\) and \(L^d\) in dry matter, and content of FeS₂ in the sandy-clay part is calculated. While changing the value of \(S^d_p\) the calculation cycle is repeated until the calculated value of FeS₂ reaches a predetermined tolerance (<0.005%). The calculation normally starts by assuming small values of \(S^d_p\) and the value increases in the calculation procedure.

Using the main calculation program (Calculation 1), the overall oil shale sulphur content and contributing subspecies will also be calculated. (An example of the calculations is presented in Appendix A.) If the calculated content of overall oil shale sulphur, compared with probable content, is out of range, then the calculation must be repeated with a new guess for content of FeS₂ in sandy-clay part.

3.3. Calculation of the chemical composition of dry fuel

The general procedure is outlined in the flowsheet below (Scheme 3).

3.3.1. Constituents contained in the organic part

To find the content of the organic chemical constituents, the composition of the typical organic part of oil shale in Table 2 and content of organic matter \((R^o)\), calculated as described before, are used. The content of any chemical constituent is calculated by the formula:

\[
G^d = G^o R^d/100
\]
where $G^d$ is the content of any constituent in dry fuel and $G^o$ is the content of any constituent in the organic part of oil shale. Consequently:

$$C^d = 0.7745R^d$$ (12)

$$H^d = 0.0970R^d$$ (13)

$$S^d = 0.0176R^d$$ (14)

$$N^d = 0.0033R^d$$ (15)

$$O^d = 0.1001R^d$$ (16)

$$Cl^d = 0.0075R^d$$ (17)

3.3.2. Constituents contained in the carbonate part

The calculation procedure is basically same as in the case of the organic part, but the basis of calculation is the composition of carbonate part (Table 2) and mass fraction of the carbonate part ($K^d$) in the oil shale. Consequently:

$$G^d = G^o K^d/100$$ (18)

and:

$$CaO^d = 0.481K^d$$ (19)

$$MgO^d = 0.066K^d$$ (20)

$$FeO^d = 0.002K^d$$ (21)

$$CO_2^d = 0.451K^d$$ (22)

3.3.3. Constituents contained in the sandy-clay part

The calculation procedure is basically same as in the previous two calculations. The content of FeS$_2$ in sandy-clay part may differ from the data given in Table 2. In the case of different contents of FeS$_2$ the contents of the other constituents of the sandy-clay part have to be recalculated accordingly (the normal composition of the sandy-clay part given in Table 2 is good only for FeS$_2 = 9.3\%$). The correction factor needed to take into account a different FeS$_2$ content, can be found using formula:

$$K_{c-rec} = (100 - FeS_2_{f-g})(100 - 9.3)$$ (23)

The contents of constituents from Table 2 have to be multiplied by a correction factor $K_{c-rec}$ to reflect the new composition:

$$G^d = G^c K_{c-rec} L^d/100$$ (24)

An exception to this is the content of FeS$_2$ itself, since this is the iteration variable and no correction factor is needed. In the case of dry fuel the contents of constituents in the sandy-clay part are calculated using the following formulas:

$$SiO_2^d = 0.598 L^d K_{c-rec}$$ (25)

$$CaO^d = 0.007 L^d K_{c-rec}$$ (26)

$$Al_2O_3^d = 0.161 L^d K_{c-rec}$$ (27)

$$Fe_2O_3^d = 0.028 L^d K_{c-rec}$$ (28)

$$TiO_2^d = 0.007 L^d K_{c-rec}$$ (29)

$$MgO^d = 0.004 L^d K_{c-rec}$$ (30)

$$Na_2O^d = 0.008 L^d K_{c-rec}$$ (31)

$$K_2O^d = 0.063 L^d K_{c-rec}$$ (32)

$$FeS_2^d = FeS_2 f-g L^d/100$$ (33)

$$SO_3^d = 0.005 L^d K_{c-rec}$$ (34)

$$H_2O^d = 0.026 L^d K_{c-rec}$$ (35)

It is because the FeS$_2$ content is so highly variable that this iterative procedure is adopted.
3.3.4. Calculation of overall sulphur content and subspecies

The content of sulphur contained in the organic part of the fuel is $S^d_o$ and this was calculated in Section 3.3.1. To find the content of pyritic (marcasite) sulphur contained in the sandy-clay part of the oil shale, on a dry fuel basis, the following formula is used:

$$S^d_p = 0.5345FeS^d_2$$

(36)

where 0.5345 is the sulphur mass fraction in $FeS_2$ and $FeS^d_2$ represents the marcasite content in fuel.

The content of sulphur present as $SO_3$ in the sandy-clay part is found using the formula:

$$S^d_{\text{ sulph}} = SO^d_3/2.5$$

(37)

The overall content of sulphur in oil shale is the sum of the three sulphur subspecies:

$$S^d = S^d_o + S^d_p + S^d_{\text{ sulph}}$$

(38)

The content of burnable sulphur in fuel ($S^d_{o+p}$) is the sum of the organic and sulphide sulphur, only.

The content of sulphur in as the received fuel is also given in the calculation table, as it is often needed. The mean moisture of fuel is taken as the basis for making a correction calculation onto an as received basis:

$$S^r = S^d (100 - W^f)/100$$

(39)

3.4. Calculation of the composition and amounts of combustion products

3.4.1. Calculation of flue gas composition and amounts

As the composition and amounts of combustion products are usually given on an as received fuel basis, the following values are calculated for as received fuel. The conversion from a dry fuel to an as received fuel basis requires a value of moisture content $W^f$. The conversion involves the following correction factor:

$$K_{dr} = (100 - W^f)/100$$

(40)

The calculation of composition and amounts of flue gas are performed according to the formulas given in Ref. [16] at a particular value of the excess-air coefficient ($\alpha$). The results are given per one kilogram of fuel. Accordingly:

Theoretical amount of air:

$$V^0 = (0.0889(C^d + 0.375S^d_{o+p}) + 0.265H^d - 0.0333O^d)K_{dr}$$

m$^3$/kg

(41)

The amount of CO$_2$ arising from burning of carbon, in m$^3$/kg:

$$V_{CO2 \text{ carbon}} = 0.01866C^d K_{dr}$$

(42)

The amount of CO$_2$ arising from decomposition of carbonates, in m$^3$/kg:

$$V_{CO2 \text{ carbon}} = 0.00509k_{CO2}(CO^d_2)K_{dr}$$

(43)

The total amount of CO$_2$, in m$^3$/kg:

$$V_{CO2} = V_{CO2 \text{ carbon}} + V_{CO2 \text{ carb}}$$

(44)

The amount of SO$_2$ arising from burning of sulphur, in m$^3$/kg:

$$V_{SO2} = 0.00702S^d_{o+p}K_{dr}$$

(45)

The amount of nitrogen (neglecting any NO$_x$ formation, which is generally small; in m$^3$/kg):

$$V_{N2} = 0.79\alpha V^0 + 0.008N^d K_{dr}$$

(46)

The amount of oxygen, in m$^3$/kg:

$$V_{O2} = 0.21(\alpha - 1)V^0$$

(47)

The amount of water vapor, in m$^3$/kg:

$$V_{H2O} = 0.111H^d K_{dr} + 0.0124W^f + 0.0161\alpha V^0$$

(48)

The total amount of flue gas, in m$^3$/kg:

$$V_g = V_{CO2} + V_{SO2} + N_2 + V_{O2} + V_{H2O}$$

(49)

The amount of dry gases, in m$^3$/kg:

$$V_{\text{dry}} = V_{CO2} + V_{SO2} + N_2 + V_{O2}$$

(50)

3.4.2. Sulphur content of burned gas

The limits of harmful components content in burned gas are established by local emission codes and calculated at standard excess air coefficient $\alpha_1$. The SO$_2$ content in the dry burned gas is calculated from:

$$g_{SO2}(\text{mg}/\text{nm}^3) = 20,000S^d_1 K_{dr} (1 - k_S)/\alpha_1 (V_{CO2} + V^0(\alpha_1 - 0.21))$$

(51)

The content of sulphur in the burned gas is calculated from:

$$SO_2(\text{ppm}) = g_{SO2}/2.860.$$  

(52)

3.4.3. Calculation of amounts of ash formed

3.4.3.1. Calculation of minimal extent of decomposition of carbonates. The carbonate part of oil shale contains MgCO$_3$ in addition to CaCO$_3$. The decomposition process of MgCO$_3$ starts at a significantly lower temperatures than the decomposition of CaCO$_3$, and because of that it is impossible to avoid decomposition of MgCO$_3$ in pressurised boilers, and the extent of carbonate decomposition, $k_{CO2}$, is always over zero. Taking into account the composition of the carbonates given in Table 2, the value of $k_{CO2}$ due to decomposition of MgCO$_3$, is $\approx 0.16$. The second reason for increasing the extent of carbonate decomposition is that
the sulphur bound by ash does not react with MgO (the latter from the decomposition process of MgCO₃), but it is only bound by CaO (even if it is bound in CaCO₃). This fact has been checked by tests carried out by DTE/TTU. Because of this, an increase in ECD caused by ash sulphation must be considered in pressurised boilers. The minimal extent of decomposition of carbonates can be thus found using the formula:

\[ k_{\text{CO}_2-\text{min}} = 1.375S_p^a/\text{CO}_2^a_M + 0.16 \]  

(53)

As the extent of decomposition of carbonate \( k_{\text{CO}_2} \) should not be less than \( k_{\text{CO}_2-\text{min}} \), the given value of \( k_{\text{CO}_2} \) should be checked and corrected as needed.

### 3.4.3.2. Percentage of constituents coming into ash from the carbonate part

In the case of constituents coming from the carbonate part into ash, oxidation of FeO into Fe₂O₃ during burning has been accounted for. The mass percentage of constituents coming from carbonate minerals into ash for dry fuel is as follows:

\[ \text{CaO} = 1.0665(\text{CO}_2^d_M) \]  

(54)

\[ \text{MgO} = 0.1463(\text{CO}_2^d_M) \]  

(55)

\[ \text{Fe}_2\text{O}_3 = 0.0049(\text{CO}_2^d_M). \]  

(56)

The total percentage of constituents coming from the carbonate part into ash (calculated for dry fuel) is as follows:

\[ K^d_{\text{ash}} = (1.0665 + 0.1463 + 0.0049)(\text{CO}_2^d_M) \]

\[ = 1.2177(\text{CO}_2^d_M). \]  

(57)

### 3.4.3.3. Percentage of constituents coming into ash from the sandy-clay part

In the case of calculation of the contribution of the sandy-clay part to the ash, it should be considered that all water of hydration vaporises and the iron of FeS₂ oxidises to Fe₂O₃ during combustion. In the case of sulphate-free ash, the SO₃ contained in the sandy-clay part is not accounted for either. A possible difference in the content of assumed FeS₂ from the content given in Table 2 is accounted for in the following calculations.

The amount of Fe₂O₃ formed from FeS₂ in the sandy-clay part (calculated for the sandy-clay part) is found by the formula:

\[ \text{Fe}_2\text{O}_3 = 0.4655\text{FeS}_2 \times 1.4297 = 0.6655\text{FeS}_2 \]  

(58)

Consequently, the percentage of the sandy-clay to be burnt to ash is as follows:

\[ L_{\text{ash}} = (100 - \text{FeS}_2 + \text{Fe}_2\text{O}_3 - (\text{H}_2\text{O} + \text{SO}_3)K_{\text{s-rec}})\]  

(59)

and the percentage of the total sulphate-free ash in the dry fuel is as follows:

\[ A^d_{\text{s-free}} = K^d_{\text{ash}} + L_{\text{ash}}L^d = 1.2177(\text{CO}_2^d_M) + L_{\text{ash}}L^d. \]  

(60)

### 3.4.3.4. Overall amount of ash in the boiler

The overall amount of ash in the boiler (kg/kg) is calculated on the as received fuel basis using the formula:

\[ A^d_{\text{boiler}} = (1.2177(\text{CO}_2^d_M) + L_{\text{ash}}L^d + (1 - k_{\text{CO}_2})(\text{CO}_2^d_M) \]

\[ + 2.5S_p^a + 0.005L^d)K_{\text{ash}}/100, \]  

(61)

where:

\[ (1 - k_{\text{CO}_2})(\text{CO}_2^d_M)—\text{accounting for an increase in ash amount because of non decomposed carbonates,} \]

\[ 2.5S_p^a + 0.005L^d—\text{increase of ash amount because of sulphur binding, and,} \]

\[ 0.005L^d—\text{increase of ash amount because of SO}_3 \text{ contained in the sandy-clay part.} \]

### 3.4.3.5. Calculation of ash composition

The contents of such constituents as SO₃, CO₂ and Cl are firing condition-dependent. It is practical to start the calculation of ash composition with a calculation for so called sulphate-free ash—for CO₂, S, SO₃ and Cl-free mass. The percentage of individual ash constituents in a sulphate-free ash is calculated using the formula:

\[ G_{\text{ash}} = (G^*K^d + G^*sK_{s-rec}L^d)/A^d_{\text{s-free}}, \]  

(62)

where in the case of constituents not present in the carbonate part, \( G^*K^d = 0 \). The content of Fe₂O₃ in the sandy-clay part \( (G^s) \) is the sum of primary Fe₂O₃ of the sandy-clay part given in Table 2 and Fe₂O₃ arising from burning of marcasite, calculated using the formula:

\[ \text{Fe}_2\text{O}_3 = 0.6655\text{FeS}_2. \]  

(63)

Calculation of the sulphate-free ash to the actual composition of ash proceeds as follows. The sulphate-free ash composition must be multiplied by a correction factor found on the basis of SO₃, CO₂ and Cl content (values obtained by chemical analysis):

\[ K_{\text{ash-rec}} = 100/(100 + \text{SO}_3 + \text{CO}_2 + \text{Cl}), \]  

(64)

where SO₃, CO₂ and Cl are the percentages of these constituents in ash according to the actual chemical analysis. If the percentage of these constituents is taken as zero, then the ash composition is calculated to the so-called sulphate-free mass.

According to this calculation method, the content of individual constituents (from the carbonate and sandy-clay part) in ash, can be found by the formulae:

\[ \text{SiO}_2 = (59.8K_{s-rec}L^d/A^d_{\text{s-free}})K_{\text{ash-rec}} \]  

(65)

\[ \text{Al}_2\text{O}_3 = (16.1K_{s-rec}L^d/A^d_{\text{s-free}})K_{\text{ash-rec}} \]  

(66)
Fe\textsubscript{2}O\textsubscript{3} = (0.49(CO\textsubscript{2})\textsubscript{M} + (2.8K_{s\text{ rec}} + 0.6655 \times FeS\textsubscript{2})L_{d}/A_{d\text{ free}})K_{ash-rec} \tag{67}

CaO = ((106.65(CO\textsubscript{2})\textsubscript{M} + 0.7K_{s\text{ rec}}L_{d})/A_{d\text{ free}})K_{ash-rec} \tag{68}

MgO = ((14.63(CO\textsubscript{2})\textsubscript{M} + 0.4K_{s\text{ rec}}L_{d})/A_{d\text{ free}})K_{ash-rec} \tag{69}

K\textsubscript{2}O = (6.3K_{s\text{ rec}}L_{d}/A_{d\text{ free}})K_{ash-rec} \tag{70}

Na\textsubscript{2}O = (0.8K_{s\text{ rec}}L_{d}/A_{d\text{ free}})K_{ash-rec} \tag{71}

TiO\textsubscript{2} = (0.7K_{s\text{ rec}}L_{d}/A_{d\text{ free}})K_{ash-rec}. \tag{72}

3.5. Calculation of amounts of ash formed and volume of flue gas per MJ

In some cases it is practical to give amounts of ash formed and volume of flue gas per MJ of heating value. Lower heating value is taken as the basis for the calculation. There are two possibilities: the assumed initial heating value (\(Q_{i}^{\text{r}}\)) or the corrected heating value (\(Q_{i\text{ correc}}^{\text{r}}\)) may be taken as the basis for the calculation. In the latter case the increase of heating value due to of non-decomposed carbonates and because of heat release caused by SO\textsubscript{2} binding by ash are taken into account. The first calculation is suitable for so-called first approximation calculations for atmospheric boilers, where the ECD (\(k_{CO2}\)) is high. The second calculation is useful for final calculations and in case of PFB boilers, where the \(k_{CO2}\) is not higher than 0.3–0.4 and the \(k_s = 1\).

In first case the amount of formed ash (\(A_{Q}^{i}\)) and volume of flue gas (\(V_{gQ}^{i}\)) per MJ is found using the formulae:

\[A_{Q}^{i} = A_{\text{boiler}}^{i}Q_{i}^{r}, \quad \text{kg/MJ} \tag{73}\]

\[V_{gQ}^{i} = V_{g}^{i}/Q_{i}^{r}, \quad \text{nm}^3/\text{MJ} \tag{74}\]

In second case the corrected heating value must be calculated, as described below.

3.5.1. Increase of heating value because of non-decomposed carbonates

The increase of heating value attributable to non-decomposed carbonates is calculated using a formula in which it is assumed that the CaCO\textsubscript{3} does not decompose:

\[
\Delta Q_{i\text{ carbon}}^{r} = (1 - k_{CO2})4.1232(CO_2)_{\text{M}}K_M/100, \text{MJ/kg}. \tag{75}
\]

3.5.2. Increase of heating value because of sulphur binding

The increase of heating value because of sulphur binding is calculated assuming formation of CaSO\textsubscript{4}. (The heat arising from formation of CaSO\textsubscript{4} is 15.616 MJ/kg of bonded sulphur. The extent of sulphur binding by ash in a calorimetric bomb is taken as 0.4 and it is accounted for when the \(Q_{i}^{r}\) was calculated. Here one has to account for additional binding only.)

\[
\Delta Q_{i\text{ sul}p}^{r} = 15.616S_{\text{M}}K_M(k_S - 0.4)/100, \text{MJ/kg}. \tag{76}
\]

According to that, the corrected heating value is found using the formula:

\[Q_{i\text{ correc}}^{r} = Q_{i}^{r} + \Delta Q_{i\text{ sul}p}^{r} + \Delta Q_{i\text{ carbon}}^{r}, \text{MJ/kg}. \tag{77}\]

3.5.3. Amount of formed ash and volume of flue gas per corrected heating value

The amount of ash formed per corrected heating value is calculated using the formula:

\[A_{Q}^{i\text{ correc}} = A_{\text{boiler}}^{i}Q_{i\text{ correc}}^{r}, \text{kg/MJ} \tag{78}\]

and volume of flue gas per corrected heating value is calculated using the formula:

\[V_{gQ}^{i\text{ correc}} = V_{g}^{i}/Q_{i\text{ correc}}^{r}, \text{nm}^3/\text{MJ}. \tag{79}\]

3.6. Heating value in a calorimetric bomb (calorific value)

Calculation 1 also recalculate the lower heating value of dry fuel to the calorific value obtained using a bomb calorimeter (\(Q_{b}^{d}\)). It allows comparing the results obtained by other methods if needed. The formulas for heating value calculations and the data concerning overall sulphur content and hydrogen content in dry fuel, given in GOST 147-74 (State standard in the former Soviet Union), are taken as a basis. The amount of ash bound by water in a calorimetric bomb is found as the ratio of overall sulphur to the bound sulphur \(n_{b-S}\). This ratio is assumed and if there are no other data for \(n_{b-S}\) the value 0.6 is recommended. The calculation is made using the formula:

\[Q_{b}^{d} = (Q_{i}^{d} + 0.0564S_{d}^{d} + 0.21831H_{d}^{d})/(1 - 0.0015). \tag{80}\]

4. Summary

A sample of Calculation 1 is given in Appendix A (Table A1).

Calculation 1 presents a quick, convenient method for estimating various performance parameters for systems firing Estonian oil shale, using minimum amount of characterization data (essentially, just heating value). While the method has been developed for a fuel resource in a geographically small area, and therefore cannot be reliably applied to oil shale from other parts of the world, some of the special considerations associated with use of this unique fuel may be generalizable.

Part 2 of this study gives oil shale calculations based on technical analysis data for cases when available initial data include \(Q_{i}^{d}, A_{i}^{d}, (CO_2)_{M}^{d}, S_{d}^{d}\) or \(Q_{i}^{r}, A_{i}^{r}, (CO_2)_{M}^{r}, S_{i}^{r}, W_{i}^{r}\). Also
Table A1
Heating value-based calculation of compositions of oil shale and product ash and amounts of ash and flue gases, formed during burning

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbol</th>
<th>Measure unit</th>
<th>Numeric values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Initial</td>
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<tr>
<td>Values assumed for calculation—not subject to iteration</td>
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<td>Values connected with fuel</td>
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<tr>
<td>Heating value of as received fuel</td>
<td>( Q_r )</td>
<td>MJ/kg</td>
<td>8.200</td>
</tr>
<tr>
<td>Content of FeS(_2) in sandy-clay part</td>
<td>FeS(_2)</td>
<td>%</td>
<td>9.30</td>
</tr>
<tr>
<td>Correction factor ( \Delta CO_2/d )</td>
<td>( \Delta CO_2/d )</td>
<td>%</td>
<td>0.00</td>
</tr>
<tr>
<td>Correction factor ( \Delta W )</td>
<td>( \Delta W )</td>
<td>%</td>
<td>0.00</td>
</tr>
<tr>
<td>Ash content in dry fuel (based on analytical calc.)</td>
<td>( A^d )</td>
<td>%</td>
<td>51.63</td>
</tr>
<tr>
<td>Values connected with operational conditions of the boiler</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Extent of carbonates’ decomposition (0–1.000)</td>
<td>( k_{CO_2} )</td>
<td>%</td>
<td>0.990</td>
</tr>
<tr>
<td>Sulphur binding rate (0–1.000)</td>
<td>( k_S )</td>
<td>%</td>
<td>0.800</td>
</tr>
<tr>
<td>—Calculated at standard excess air coefficient</td>
<td>( a_1 )</td>
<td></td>
<td>1.40</td>
</tr>
<tr>
<td>Overall coefficient of excess air in boiler</td>
<td>( \alpha )</td>
<td></td>
<td>1.60</td>
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<tr>
<td>Calculation of mean constituents of fuel—subject to iteration</td>
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<td>Determining carbonate CO(_2), moisture and ash contents</td>
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</tr>
<tr>
<td>Calculated moisture content of as received fuel</td>
<td>( W_r^\text{calc} )</td>
<td>%</td>
<td>11.40</td>
</tr>
<tr>
<td>Corrected moisture content</td>
<td>( W_r^\text{calc} )</td>
<td>%</td>
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<tr>
<td>Heating value of dry fuel</td>
<td>( Q_d )</td>
<td>MJ/kg</td>
<td>9.570</td>
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<td>Calculated content of ( CO_2/d )</td>
<td>( CO_2/d )</td>
<td>%</td>
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</tr>
<tr>
<td>Corrected content of ( CO_2/d )</td>
<td>( CO_2/d )</td>
<td>%</td>
<td>20.33</td>
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<tr>
<td>Calculated ash content</td>
<td>( A^d )</td>
<td>%</td>
<td>51.63</td>
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<tr>
<td>Content of main constituents (calculated by Macro)</td>
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<tr>
<td>Mass percentage of carbonate components</td>
<td>( K^d )</td>
<td>%</td>
<td>45.07</td>
</tr>
<tr>
<td>Mass percentage of organic components</td>
<td>( R^d )</td>
<td>%</td>
<td>29.49</td>
</tr>
<tr>
<td>Mass percentage of sandy-clay components</td>
<td>( L^d )</td>
<td>%</td>
<td>25.44</td>
</tr>
<tr>
<td>Total: ( K^d + R^d + L^d )</td>
<td></td>
<td>%</td>
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</tr>
<tr>
<td>Calculation of chemical composition of dry fuel</td>
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</tr>
<tr>
<td>Constituents of organic part</td>
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</tr>
<tr>
<td>Content of carbon</td>
<td>( C^d )</td>
<td>%</td>
<td>22.84</td>
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<tr>
<td>Content of hydrogen</td>
<td>( H^d )</td>
<td>%</td>
<td>2.86</td>
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<td>Content of organic sulphur</td>
<td>( S^d )</td>
<td>%</td>
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</tr>
<tr>
<td>Content of nitrogen</td>
<td>( N^d )</td>
<td>%</td>
<td>0.10</td>
</tr>
<tr>
<td>Content of chlorine</td>
<td>( Cl^d )</td>
<td>%</td>
<td>0.22</td>
</tr>
<tr>
<td>Content of oxygen</td>
<td>( O^d )</td>
<td>%</td>
<td>2.95</td>
</tr>
<tr>
<td>Total</td>
<td>( R^d )</td>
<td>%</td>
<td>29.49</td>
</tr>
<tr>
<td>Constituents of carbonate part</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Calcium oxide</td>
<td>CaO(_d)</td>
<td>%</td>
<td>21.68</td>
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<tr>
<td>Magnesium oxide</td>
<td>MgO(_d)</td>
<td>%</td>
<td>2.97</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>FeO(_d)</td>
<td>%</td>
<td>0.09</td>
</tr>
<tr>
<td>Carbonate CO(_2)</td>
<td>CO(_2/d)</td>
<td>%</td>
<td>20.33</td>
</tr>
<tr>
<td>Total</td>
<td>( K^d )</td>
<td>%</td>
<td>45.07</td>
</tr>
<tr>
<td>Constituents of sandy-clay part</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Correction factor to other content of FeS(_2)</td>
<td>( K_{Fe \text{rec}} )</td>
<td></td>
<td>1.000</td>
</tr>
<tr>
<td>Silica oxide</td>
<td>SiO(_2/d)</td>
<td>%</td>
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<tr>
<td>Calcium oxide</td>
<td>CaO(_d)</td>
<td>%</td>
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<tr>
<td>Aluminium oxide</td>
<td>Al(_2)O(_3/d)</td>
<td>%</td>
<td>4.10</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>Fe(_2)O(_3)</td>
<td>%</td>
<td>0.71</td>
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<td>Titan oxide</td>
<td>TiO(_2)</td>
<td>%</td>
<td>0.18</td>
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<tr>
<td>Magnesium oxide</td>
<td>MgO(_d)</td>
<td>%</td>
<td>0.10</td>
</tr>
<tr>
<td>Sodium oxide</td>
<td>Na(_2)O(_d)</td>
<td>%</td>
<td>0.20</td>
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<td>Potassium oxide</td>
<td>K(_2)O(_d)</td>
<td>%</td>
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<td>Marcasite</td>
<td>FeS(_2)</td>
<td>%</td>
<td>2.37</td>
</tr>
<tr>
<td>Sulphate sulphur</td>
<td>SO(_3/d)</td>
<td>%</td>
<td>0.13</td>
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<tr>
<td>Crystal water</td>
<td>H(_2)O(_d)</td>
<td>%</td>
<td>0.66</td>
</tr>
<tr>
<td>Total</td>
<td>( L^d )</td>
<td>%</td>
<td>25.44</td>
</tr>
</tbody>
</table>

(continued on next page)
### Table A1 (continued)

<table>
<thead>
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<th>Numeric values</th>
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<tbody>
<tr>
<td></td>
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<td>Initial</td>
</tr>
<tr>
<td>Total $K^d + K^d + L^d$</td>
<td>%</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Calculation of content of total sulphur and its constituents</td>
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<td></td>
</tr>
<tr>
<td>Organic sulphur</td>
<td>$S^d_o$</td>
<td>%</td>
<td>0.52</td>
</tr>
<tr>
<td>Pyrite (marcasite) sulphur</td>
<td>$S^d_p$</td>
<td>%</td>
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</tr>
<tr>
<td>Sulphate sulphur</td>
<td>$S^d_{sulph}$</td>
<td>%</td>
<td>0.05</td>
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<tr>
<td>Total sulphur</td>
<td>$S^d_t$</td>
<td>%</td>
<td>1.83</td>
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<tr>
<td>$S^d_o + S^d_p$</td>
<td>%</td>
<td>1.78</td>
<td>1.79</td>
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<tr>
<td>Content of total sulphur in fuel as received</td>
<td>$S^d_r$</td>
<td>%</td>
<td>1.63</td>
</tr>
</tbody>
</table>

### Calculation of composition and amounts of combustion products

Calculation of composition and amounts of combustion gases (at selected $a$ values)

- Recalculation factor for as received fuel $K_{dr}$
  - 0.8860
  - 0.8846
  - 0.8833
- Theoretical amount of air needed for burning $V^o$
  - nm$^3$/kg
  - 2.44
  - 2.49
  - 2.54
- Amount of CO$_2$ formed by burning of carbon $V_{CO2}^{carbon}$
  - nm$^3$/kg
  - 0.38
  - 0.39
  - 0.39
- Amount of CO$_2$ formed by decomposition of carbonates $V_{CO2}^{carb}$
  - nm$^3$/kg
  - 0.09
  - 0.09
  - 0.09
- Total amount of CO$_2$ $V_{CO2}$
  - nm$^3$/kg
  - 0.47
  - 0.48
  - 0.48
- Amount of SO$_2$ formed by burning of sulphur $V_{SO2}$
  - nm$^3$/kg
  - 0.01
  - 0.01
  - 0.01
- Amount of nitrogen $V_{N2}$
  - nm$^3$/kg
  - 3.08
  - 3.14
  - 3.21
- Amount of oxygen $V_{O2}$
  - nm$^3$/kg
  - 0.31
  - 0.31
  - 0.32
- Amount of water vapour $V_{H2O}$
  - nm$^3$/kg
  - 0.49
  - 0.49
  - 0.50
- Total amount of CO$_2$ $V_{g}$
  - nm$^3$/kg
  - 4.35
  - 4.44
  - 4.53
- Amount of dry gases $V_{dry}$
  - nm$^3$/kg
  - 3.87
  - 3.94
  - 4.02
- Sulphur content in flue gas (at assumed $a$ values)
  - Content of SO$_2$ $r_{SO2}$ mg/nm$^3$
    - 1931
    - 1898
    - 1868
  - Recalculated as ppm SO$2$
    - 675
    - 664
    - 653
- Calculation of amount of ash formed
  - Minimal extent of carbonates’ decomposition $k_{CO2-min}$
    - 0.256
    - 0.258
    - 0.260
  - Amount of constituents going into ash:
    - From carbonate part (% of fuel) $k_{carbon}$
      - 24.75
      - 24.43
      - 24.08
    - From sandy-clay part (% of fuel) $k_{clay}$
      - 23.86
      - 23.78
      - 23.73
  - Amount of formed sulphate-free ash $A_{s-free}^d$
    - %
    - 48.61
    - 48.21
    - 47.82
  - Total amount of ash formed in boiler $A_{d}$
    - kg/kg
    - 0.465
    - 0.461
    - 0.457
- Calculation of sulphate-free ash composition
  - Silicon dioxide SiO$_2$
    - %
    - 31.29
    - 31.45
    - 31.65
  - Aluminium oxide Al$_2$O$_3$
    - %
    - 8.43
    - 8.47
    - 8.52
  - Iron oxide Fe$_2$O$_3$
    - %
    - 4.91
    - 4.93
    - 4.96
  - Calcium oxide CaO
    - %
    - 44.95
    - 44.74
    - 44.34
  - Magnesium oxide MgO
    - %
    - 6.33
    - 6.30
    - 6.26
  - Potassium oxide K$_2$O
    - %
    - 3.30
    - 3.31
    - 3.33
  - Sodium oxide Na$_2$O
    - %
    - 0.42
    - 0.42
    - 0.42
  - Titanium dioxide TiO$_2$
    - %
    - 0.37
    - 0.37
    - 0.37
  - Total
    - %
    - 100.00
    - 100.00
    - 100.00

### Corrected values of ash content and amount of gases

Calculated for assumed initial heating value

- Ash amount $A_{0}$
  - kg/MJ
  - 0.057
  - 0.055
  - 0.053
- Amount of flue gas $V_{flue}$
  - nm$^3$/MJ
  - 0.531
  - 0.528
  - 0.526

Calculated for corrected heating value

- Correction factor for undecomposed carbonates $\Delta Q_{c-c}$
  - MJ/kg
  - 0.007
  - 0.007
  - 0.007
- Correction factor for sulphur binding $\Delta Q_{sulph}$
  - MJ/kg
  - 0.099
  - 0.099
  - 0.099
- Corrected heating value $\Delta Q_{correc}$
  - MJ/kg
  - 8.306
  - 8.506
  - 8.707
- Reduced ash amount $A_{correc}$
  - kg/MJ
  - 0.056
  - 0.054
  - 0.052
- Reduced amount of flue gas $V_{flue-corr}$
  - nm$^3$/MJ
  - 0.524
  - 0.522
  - 0.520

### Heating value in calorimetric bomb

- Ratio of bomb water sulphur to total sulphur $m_{w-s}$
  - Assumed
  - 0.60
  - 0.60
  - 0.60
- Heating value in the calorimetric bomb $Q_{b}$
  - MJ/kg
  - 10.313
  - 10.573
  - 10.833
comparison of results of other calculation methods used for Estonian oil shale calculation is presented.

Acknowledgements

The authors of this work gratefully acknowledge for the advice and support Prof. Eric Suuberg in preparing the presentation in this work.

Appendix A. Sample calculation

Table A1

References

[10] A letter from Eesti Põlevkivi Ltd to Estonian Power Plant—03.04.98. no. 6/5-5-257. Long-term prognosis of oil shale heating value changes up to year 2020 (in Estonian).