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ACTIVATION OF OIL SHALE ASHES FOR SULFUR CAPTURE

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Abstract. *Ash reactivation technology using the Szego Mill™ for grinding ashes with water, previously presented*[**] *at the Clearwater Clean Energy Conference in Florida, USA, June 2018, is now being applied to the activation of ashes from oil shale combustion.*

For coal ashes, typically from fluidized bed combustion (FBC), limestone has been added as a source of calcium. In typical oil shales, there is a great deal of calcium carbonate present naturally. In an FBC boiler, there is enough time for sulfur adsorption, but with pulverized firing, that is not the case. Thus, it is necessary to remove the sulfur dioxide from the flue gases.

At the Eesti Power Plant in Narva, Estonia, the Alstom-developed Novel Integrated Desulfurization (NID) reactor system is used and some additional lime is added since much of the original calcium has been encapsulated at the high combustion temperature in the furnaces. Several tests using cyclone ash from that plant, activated with the Szego Mill, have been carried out with good results. The initial publication has compared the characteristics of activated ash and commercial lime and established their importance for sulfur capture. The performance results indicate that, per unit free CaO, well-activated ash is at least as good as the purchased lime, but three times more is needed due to the lower CaO content.

Further testing is planned, both in the laboratory and, it is hoped, also at the Power Plant in Narva. As use of oil shale is increasing in various countries, the results anticipated should find broader utilization.

Keywords: *oil shale ashes, ashes activation, sulfur capture, flue gases.*

1. Introduction

Kukersite oil shale is the major fuel used for power generation in Estonia. That shale has a relatively low calorific value, 8–10 MJ/kg, and high mineral

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[TM] Szego Mill™ is a trademark of General Comminution Inc. for its planetary ring-roller mills.
[**] Presented by the Corresponding Author of the current paper.

content, 65–70%, with carbonates and sandy-clay minerals in about equal amounts. It is used both in circulating fluidized beds (CFB) – where all SO_2 is readily captured – and in furnaces with powdered firing. The relevant technology is thoroughly described by Ots [1].

For capture of the emitted SO_2 in the flue gas, the Alstom semi-dry DeSOx system, Novel Integrated Desulfurization System (NID), has been installed on four power units, 180 MWel each, at the Eesti Power Plant. To guarantee a deeper binding of SOx, in addition to the ashes in the flue gas, also commercial lime is added as a binding agent. In order to assess the possibility of replacing that added lime with activated ash, a study was undertaken at Tallinn University of Technology comparing performance of the two adsorbents for SO_2 binding. The results reported [2] were most encouraging and will be partially reviewed later.

As most attendees at the Clean Energy Conference in Florida, USA, June 2018, are not familiar with oil shale as a fuel, a brief description of its properties, availability and uses is given next.

2. Oil shales

Extensive research has been carried out on oil shale during the last century, much of it in Estonia. Most of the recent efforts have been described in the journal "Oil Shale" published by the Estonian Academy Publishers in Tallinn since 1983. That Journal has recently initiated a new series called "Historical Reviews". The first of these, by Harvey [3], describes the shale-oil industry in Scotland where the first commercially successful production of oil from shale was undertaken.

Scotland, apparently, was the global pioneer of the modern oil industry and, for a few decades in the second half of the 19th century, the leading oil producer in the world. All that was based on oil shale as feedstock!

Interestingly, shale oil production peaked there during World War I, at 27 million barrels per annum, in 1913. A significant number of byproducts were also made, for example mothballs and candles.

While oil shale is mined and utilized in several countries, China, Turkey, Iran and many others, the oil shale industry in Estonia is currently the most developed in the world. This is particularly the case in power plants but also in other respects, such as retorting. The oil shale being mined and utilized is the kukersite shale, often referred to simply as "Estonian oil shale". Urov and Sumberg [4] offer an overview of oil shales in Estonia and compare these with deposits elsewhere in the world. Raukas and Punning [5] point out that over one billion tonnes of oil shale has been produced in Estonia, the largest producer and consumer in the world since the 1960s. They do also point out the serious environmental problems which have arisen from such intensive exploitation of the resource and describe some remedial steps being taken.

The organic matter in oil shale is called kerogen. It has been formed from protista, bacteria, algae and plankton, mostly unicellular marine organisms. As a result, there are no intercellular bonds and the main consolidating substance in the fuel is fat from the original material. As kerogen is of sapropelic origin – from original marine sources – it has a low solubility in solvents and is characterised by high hydrogen and oxygen content. The atomic H/C ratio is about 1.5, approximately the same as in crude oil.

While the mineral matter in shales may vary greatly both in composition and in the amounts present, the kerogen part, originating largely from similar organisms, is reasonably consistent and does not depend on the total amount of kerogen contained. This is in contrast to the humic fuels where many different plant species have gone into forming the peat, lignite or coal deposits.

The average chemical composition of the kerogen may be represented by the empirical formula: $C_{10}H_{15}OCl_{0.03}S_{0.07.}$

There are two large groups of minerals in oil shale, viz. a carbonate part and a sandy-clay part in about equal amounts. The sandy-clay part is mainly, about 60%, SiO_2 with Al_2O_3 at 16%. The carbonate minerals are mostly, about 70%, calcite, $CaCO_3$ with dolomite, $CaMg\ (CO_3)_2$ making up the remainder.

Some further information is provided by Trass [6] and a great deal more is available in the book on Oil Shale Combustion by Ots [1].

3. Ash reactivation

The basic idea arose from the fluidized bed combustion of high sulfur coal or petroleum coke. When such fuels are burned, the sulfur oxides released must be captured. This is done by adding limestone, typically as calcite or dolomite, to the bed which provides both thermal stability and a means for in situ sulfur capture. Limestone is first calcined:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 182.1 \text{ kJ/mol}$$

and then sulphated:

$$CaO + SO_2 + \tfrac{1}{2}\, O_2 \rightarrow CaSO_4 \qquad \Delta H = -481.4 \text{ kJ/mol}$$

Limestone is calcined completely, but only 30–40% is sulfated. Thus, if the remaining calcium oxide can be reused, there will be an energy saving (the calcination reaction is endothermic), less limestone will be consumed, less carbon dioxide produced and less ash to be disposed of. This summarizes the incentives for ash, or sorbent reactivation.

The main reason for the observed low sulfation levels is the fact that the molar volume of sulfate is larger than that of oxide or carbonate. As sulfation proceeds, this leads to pore plugging and the formation of an eventually impenetrable $CaSO_4$ shell surrounding a substantially unreacted CaO core.

Many factors enter in both the initial calcium utilization in fluidized bed combustion (FBC) systems as well as the efficacy of regeneration. The broad topic is thoroughly presented in a review paper by Anthony and Granatstein [7]. They discuss the mechanisms of the sulfation reaction, emphasize what is known about sulfur capture in FBC boilers, and briefly cover the topic of sorbent reactivation. Also, it has been established that complete hydration will produce the most reactive regenerated sorbent.

The process proposed here [8] again involves grinding the ashes with excess water to initiate hydration, involving both mechanical action and excellent contacting of the just-created surfaces with water. The hydration reaction

$$CaO + H_2O(l) \rightarrow Ca(OH)_2 \qquad \Delta H = -65.3 \text{ kJ/mol}$$

is exothermic and, once initiated, will proceed rapidly to completion. If that wet mixture is allowed to stand, it will undergo slower, self-cementing reactions and harden. To avoid that, a number of steps can be taken. These include adding, after some appropriate time, limestone, ash or coal, all dry, to the wet mixture. The resulting substantially dry mixture would then be granulated and the self-cementing reactions would simply help to keep the granules strong enough for subsequent ease of handling.

It is also possible to use less water so that grinding is done on the "dry side", with just enough water for hydration. This does greatly simplify the operation as it makes the mixing/drying step unnecessary.

This process has been tested with coal ashes at the pilot scale and also in two 35 MWth utility boilers [8, 9] and has also been patented [10]. Summaries of that work have also been presented by Trass at the International Technical Conference on Clean Coal & Fuel Systems, Clearwater, Florida, with the latest in 2016 [11].

A key piece of equipment for the process is the Szego Mill^{TM}, a planetary ring-roller mill with helically grooved rollers developed at the University of Toronto [12]. This mill can be used for both dry and wet grinding. Its special niche is grinding wet at high solids concentrations, when the material is paste-like and has a very high viscosity. This is the case because the roller grooves help to push the material through the mill. Most other mills lose both capacity and grinding efficiency under those conditions whereas the Szego Mill^{TM} continues to perform well. For the experiments described earlier, the SM-320 mill (320 mm inside diameter) with four rollers was used. A schematic diagram of the Szego Mill^{TM} is given in Figure 1.

Previous test work had been carried out in a pilot plant CFBC, 0.1 m in diameter and 5.5 m high (0.8 MWt), located at the CANMET Energy Technology Centre in Nepean, Ontario. The initial utility boiler tests were carried out at the Wade Utility Plant (35 MWt) of Purdue University, Lafayette, Indiana. Detailed results from both are reported by Anthony et al. [9] and summarized by Trass [13].

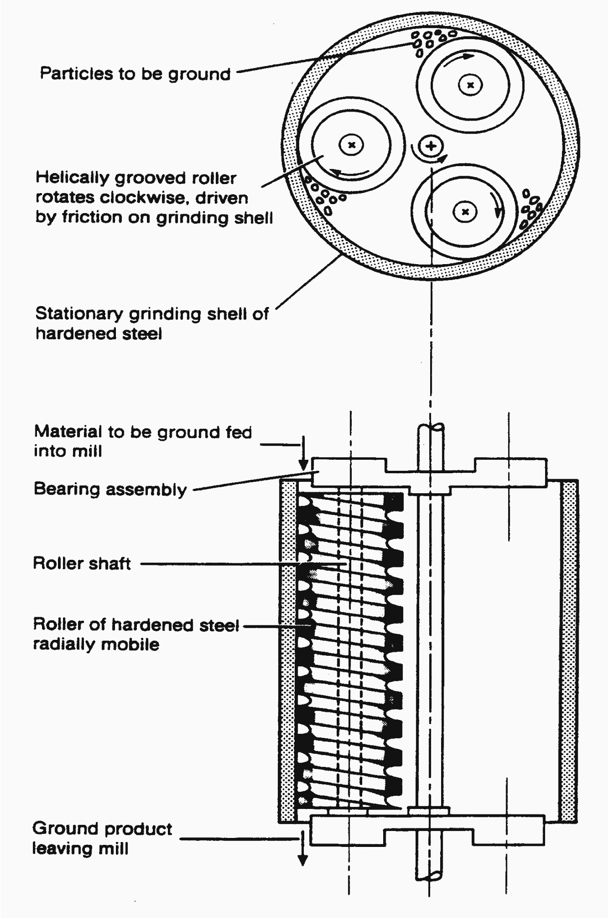

Fig. 1. A schematic diagram of the Szego Mill^{TM}.

A subsequent test series was carried out at the power plant of the Southern Illinois University, Carbondale, Illinois, in collaboration with The Babcock and Wilcox Company [8]. For on-line operation at the plant, the full capacity of the SM-320 mill could not be utilized; feed rates to the mill were about 800 kg/h or less, whereas the previously used capacity had been up to 3 tonnes per hour [9].

The issue of operating on the "dry" or "wet" side arises from the fact that the wet ashes are very sticky, and even the Szego Mill cannot operate reliably in the region of about 10% to 25% water addition. The wet ashes are not only sticky but the cementitious reactions and the resultant hardening of the material may start in the mill if the tail end of the residence time is too long. On the "dry" side, material behaves as a slightly moist powder flowing out readily and not sticking. On the "wet" side, there is enough water to slurry the ash and all of it will flow and be pushed by the roller grooves out of the mill sufficiently rapidly.

To sum up the results presented previously, it has been shown that, of the calcium hydroxide, $Ca(OH)_2$, formed by hydration, at least 60–70% was converted to sulphate. That compares with the 30–40% utilization of the calcium in the added limestone. Hydration levels vary with the processing conditions, but, once hydrated, the hydroxide is consistently quite reactive. Comparison of data from different test programs and by various authors is presented by Trass et al. [8] and most recently by Trass at the 2016 Clearwater Conference [11] to reach the above conclusion.

4. Activation and testing of oil shale ashes

At the Eesti Power Plant in Narva the flue gases go through cyclones before entering the NID reactors. About one third of the ashes is separated there, with the finest filtered out leaving the NID units. Those cyclone ashes used in the test work had a median particle size of 63 μm and a free CaO content of 26% and were deemed to be the most appropriate ash for activation.

SO_2 adsorption tests were carried out using the original, unprocessed ash, dry ground ash and "semi-dry" ground ash, with 5% and 7% water added during grinding with the Szego Mill. A higher water addition caused feeding problems with the particular mill used. Subsequently, widening the inlet system readily allowed the addition of nine or ten percent water needed for substantially complete hydration of the free oxide, but no comparative test results are available.

Kaljuvee et al. [2] give a great deal of information about measured sample properties as well as SO_2 adsorption rates and amounts. Adsorption tests covered the temperature range from 80 ºC to 700 ºC.

The important SO_2 adsorption work was carried out using the Setaram Labsys 2000 thermoanalyzer under isothermal conditions with 1 mol% sulfur dioxide in nitrogen. The gas mixture was led to the reaction chamber with a flow rate of 20 mL/min during 45 minutes. A Pt-multiplate crucible was used with 80+/–0.5 mg samples.

The lowest, 80 ºC temperature was chosen because the Alstom DeSOx (NID) system operates at that temperature. Let us, then, look at some of the 80 ºC results.

We note in Figure 2a that the binding capacity of the initial, untreated ash was poor. The other ashes and lime showed a more rapid initial rate and higher values over all of the 45 minutes. The hydrated lime showed a more rapid rate and a much higher binding level was attained compared to dry lime. This indicates the obviously much higher rate of reaction between the calcium hydroxide and SO_2 compared to adsorption or binding of SO_2 by calcium oxide. This observation lines up well with the coal ash results where, again, the hydroxide has a greater adsorption capability than the calcined limestone, that is, calcium oxide.

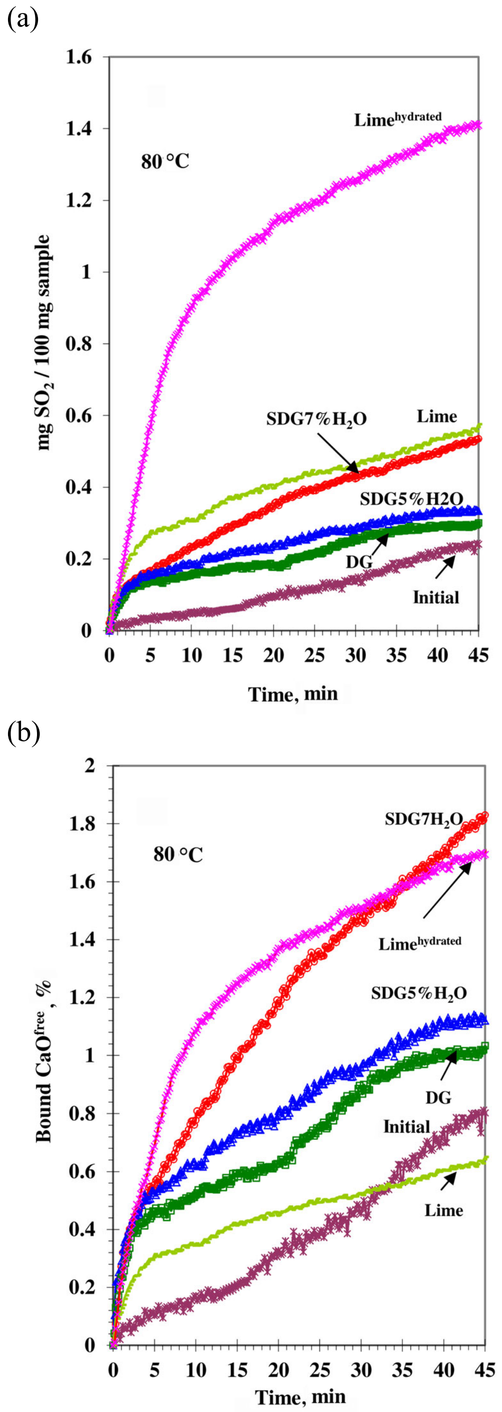

Fig. 2. Dependence of SO_2 binding capacity of sorbents on contact time between solid and gaseous phases at 80 °C: (a) mg SO_2/100 mg of sample**,** (b) mg CaO utilized/100 mg of free CaO in sample, %.

Looking at Figure 2b, the same data are given on a unit of free CaO rather than sample weight basis. The lime sample had a CaO content of 77.4%, almost exactly three times higher than measured in the ash. Thus, proportions change accordingly. The 7% water-treated ash lines up reasonably with the hydrated lime and the dry-ground ash beats the lime.

One might have expected the 5% water-treated ash to be closer to the 7% one than to the dry-ground ash. It is possible that the added water was not as well dispersed in the Szego Mill as expected, i.e. that the small samples taken may not be fully representative. The 7% sample may well have come from a better moisturised part of the mill product, and the opposite may be the case for the 5% water sample. New work will have a more uniform dispersal of the water added to the mill.

When we compare sample properties to their performance, we note in [2] that the best correlation is with total pore volume (mm³/g) and, secondly, with the BET surface area (m²/g). The pore volume relationship is shown in Figure 3, for the 45 minute values.

For the purpose of this paper, only the 80 ºC temperature data are important. Experiments were also carried out at higher temperatures, viz. 300, 400, 500 and 700 ºC. Those results are shown in Figure 4 for the 45 minute contact time. It is surprising to see the lime results behaving quite differently from the ash data. At 300 ºC, the hydrated lime does twice as well as the best, 7% water-activated ash. At higher temperatures things reverse and, at 700 ºC, even the untreated original ash performs better than the hydrated lime and the 7% water-activated ash adsorbs almost twice as much SO_2 as does the hydrated lime.

There is a great deal more information given in [2]. The suggestion is made there that such activated ashes, because of their good performance at high temperatures, could be used also for injection directly into the boiler

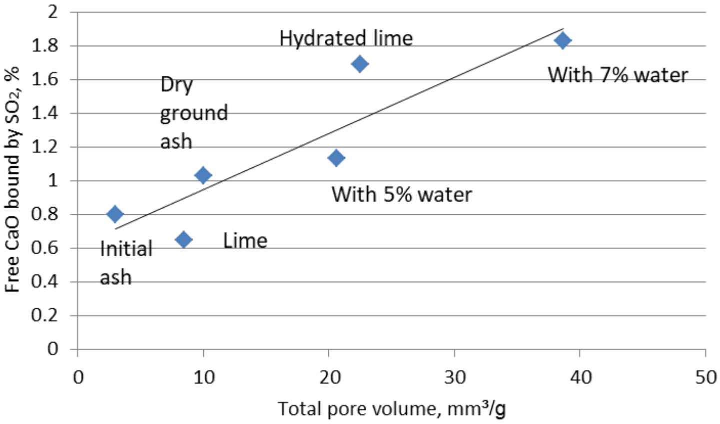

Fig. 3. Dependence of SO_2 binding efficiency (%) of sorbents on total pore volume (mm³/g) at 80 ºC after 45 min contact.

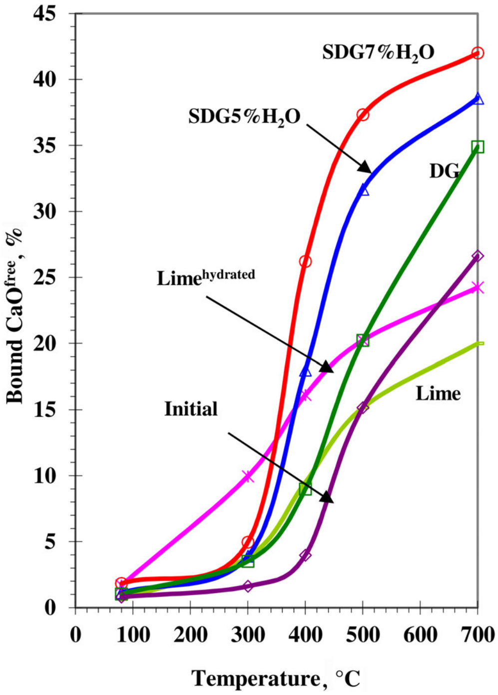

Fig. 4. Dependence of SO_2 binding efficiency (%) of sorbents on experiment temperature after 45 min contact between solid and gaseous phases.

gas tract. As expected, the paper concludes that activated ashes, particularly at higher water levels, can readily replace the commercial lime used in the NID reactors.

Subsequent work on this topic has dealt with improvement of grinding conditions for more uniform water distribution and higher water levels. As, stoichiometrically, 9% of water was needed for complete hydration for the ash used, it may be estimated that perhaps two thirds of the CaO was hydrated at the 7% water level. Thus, there is considerable room for improvement.

An issue to be faced at the Power Plant is the need to cool the ashes. The cyclones discharge ash at about 200 ºC and it must be cooled well below the reactor temperature of 80 ºC since the hydration reaction is strongly exothermic and, hence, temperature rises again.

The alternative approach is to use a great deal more water so that separate cooling would not be needed. Then the wet, fully hydrated ashes should be pumped as slurry directly into the reactors where water is being added to cool down the flue gas and the fly ash it contains.

Another question has arisen in connection with the potential Power Plant tests and implementation – that of equipping each individual NID reactor with its ash activation equipment line or to set up a more central facility. For the former, excess water can be used, the SM-320 mill would have the appropriate capacity, with the ash slurry pumped to the reactor. For a central system, only the “dry” side grinding would be allowed since the activated ash would have to be stored. Larger mills may be used and, in that case, the existing lime storage and distribution system could be utilized for getting the activated ashes to each reactor, as needed.

5. Conclusions

Electricity production in Estonia is based mainly on the pulverized firing of kukersite oil shale which has a high content of carbonate mineral matter. To capture the SO_2 in the flue gas, Alstom DeSOx novel integrated desulfurization systems have been installed and, for improved SO_2 capture, commercial lime is added to the reactor.

Regeneration of ashes from fluidized bed combustion boilers burning coal and/or coke with limestone addition for sulfur capture have shown that calcium hydroxide is considerably more reactive than the oxide and, hence, hydration is an essential part of ash reactivation. Following that example, some work on the activation of oil shale ashes has been carried out with good results.

The possibility to replace the commercial lime with activated ash has been shown. Various alternatives for such replacement at the Eesti Power Plant in Narva, Estonia, are being considered and, hopefully, will be implemented. Prior to that, further work, particularly that of testing performance of the Szego Mill in actual, longer term operation, is required.

Acknowledgement

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