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ASH UTILIZATION AFTER COMBUSTION AND THERMAL PROCESSING OF ESTONIAN (KUKERSITE) OIL SHALE

Demands on Ash Quality

The amount of mineral matter in the fuel, as well as the type of mineral matter (siliceous, aluminous or carbonaceous) and the content of sulphur, chlorine, phosphorus, rare and heavy metals, etc., determine jointly, with the thermal treatment and mineral wastes handling technologies, the properties (quality) of the resulting solid residue of fuels. Considering the availability of different technologies on the utilization of oil shale, it is indispensable that the solid wastes should meet the following requirements.

Minimum demand — the wastes stored (buried) in ash dumps, lagoons or other disposal areas should cause no risk to the environment.

Maximum demand — the solid wastes should possess the qualities to ensure their complete utilization in industry, civil engineering and agriculture.

The most complicated problem is the harmless disposing and reclamation of disposal areas of wastes not completely oxidized on thermal processing and containing carbon, water-soluble sulphides, carcinogenic polycyclic aromatic hydrocarbons, phenols and other products of pyrolysis.

For a good result the leaching of metals in water from the solid wastes must be as low as possible.

Mineral matter of kukersite oil shale and its utilization are discussed by V. H. Kikas [1].

The present paper is not decided to discuss the problems on technologies of utilization of ash or other solid residue from combustion and processing of oil shale. It will discuss some problems touching upon the utilization technologies of oil shale from the standpoint of the utilization and environmental safety of the solid residue.

Combustion Ashes

Pulverized Oil-Shale Ashes. The main technology of combustion of oil-shale in power stations is the pulverized fuel combustion. About 60... 80 per cent of the resulting ash is carried out of the furnace with the combustion gases in the form of finest powder and is known as fly-ash, also pulverized fuel ash. The fly-ash is ordinarily precipitated in inertial (cyclone) and electrical precipitators.

The remainder part of ash falls to the bottom of the furnace as a coarser material known as furnace bottom ash.

Pulverized low-grade coal, lignite or oil-shale are injected into the furnace in a stream of hot air, where it is burnt instantaneously at tem-

peratures of about 1500...1750 K. As a result, the shale minerals undergo various chemical destructions, associating to clinker minerals, conversion into plastic, liquid and volatilized stages depending on temperature, fineness of grinding and retention periods within zones with different temperature and gaseous atmosphere of the furnace.

The effect of different chemical and physical changes which various size and type mineral particles undergo (clay, sand and carbonate minerals) is demonstrated on the selective composition of coarse bottom ash, various fractions of fly-ash and residual ash in exit gas from pulverized oil shale 100 MW boiler unit.

The boiler is equipped with a cyclone and four-fielded electrostatical precipitators installed in succession (Fig. 1). The fuel and ash samples were taken and analysed by L. I. Pets *et al.* [2] in Tallinn and Leningrad, also Gehstadt (West Germany). Sulphur and iron occur mainly in pyrite (or markasite), silicium in quartz, also in clay minerals and feldspars. The very fine-grained clay minerals, also feldspars are the main bearers of aluminium and potassium. Calcium of the oil shale occurs from coarser limestone particles.

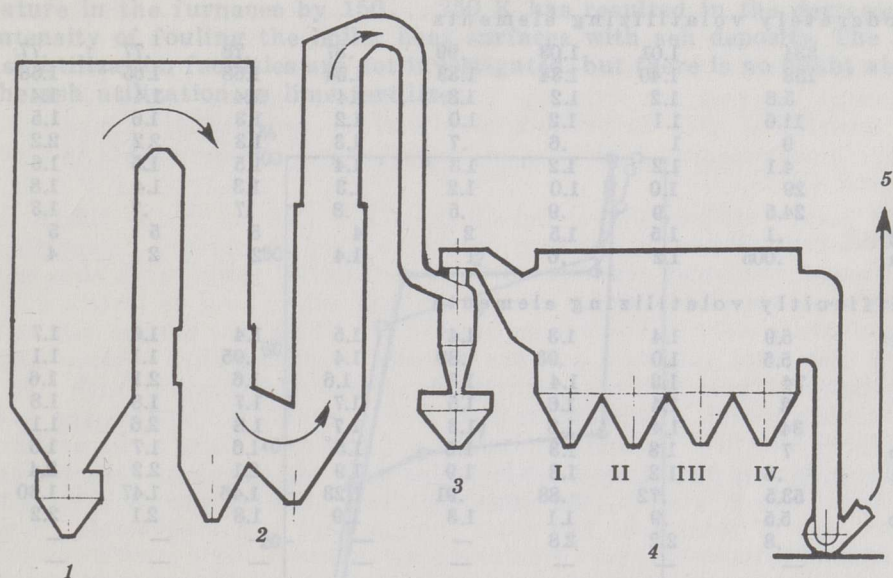


Fig. 1

Scheme of ash samples: 1 — furnace bottom ash, 2 — gas duct ash, 3 — cyclone ash, 4 — electrostatical precipitator ashes, 5 — fly-ash from exit gas

With such a composition of the inorganic matter of the pulverized oil-shale, it is law-governed that fly-ash, particularly the finest fractions of the fly-ash are concentrated with aluminium, silicium and alkali metals and impoverished on calcium and magnesium as demonstrated in [2]. The relatively higher concentration of potassium in the finest ash (precipitator fields II, III and IV and fly-ash in exit gas) is interpreted also as a result of thermal destruction of clay minerals in the furnace with volatilizing of potassium [2].

Table demonstrates volatilizing of several trace elements and their quantities in ash fractions. Concentration of some moderate and difficult volatilizing elements in the ash from the last fields of electrostatical precipitator and exit gas after gas cleaning as to be seen in Table is explicable with their origin from finest clay minerals.

Trace Elements in Pulverized Oil-shale Ash Fractions
in Coefficients to Bottom Ash (after L. I. Pets et al. [2])

Element	Bottom ash, g/t	Fly-ash precipitated in				Fly-ash passing precipitator		
		Gas duct	Cyclone	Electrostatical precipitator field				
				I	II		III	IV
Easily volatilizing elements								
As	9.16	0.91	0.81	1.99	3.14	3.53	4.12	4.93
Sb	.23	1.15	1.17	1.51	3.20	3.46	4.29	3.96
Se	.1	2	1.5	3	10	9.5	7	6
Cl	300	1.7	5.3	5.9	12.9	13.8	15.3	23.0
Br	23.6	1.18	5.7	9.5	22.9	27.1	32.2	29.0
Rb	42.5	1.48	1.35	1.62	2.82	3.15	3.70	3.95
Cs	1.81	1.7	1.40	2.24	4.4	5.2	5.72	5.97
Pb	13	3.0	4.3	3.2	7.5	8.7	9.5	12.6
Zn	81.5	.88	.75	.87	1.4	1.66	1.72	2.25
Cd	—	1	.3	—	—	—	—	—
Hg	<.1	1	1	1	1	1	1	1
Moderately volatilizing elements								
Sr	334	1.01	1.03	.99	.87	.78	.77	.77
Ba	153	1.40	1.34	1.33	1.54	1.68	1.65	1.68
Sc	5.8	1.2	1.2	1.3	1.4	1.4	1.4	1.4
Y	11.6	1.1	1.2	1.0	1.2	1.3	1.6	1.5
Ga	9	1	.6	.7	1.3	1.3	2.2	2.2
Co	4.1	1.2	1.2	1.3	1.4	1.5	1.5	1.6
Ni	29	1.0	1.0	1.2	1.3	1.3	1.4	1.8
Cu	24.5	.9	.9	.5	.8	.7	.7	1.3
Ag	.1	1.5	1.5	2	4	5	5	5
Au	.005	1.2	.6	1	1.4	2	2	4
Difficultly volatilizing elements								
Th	5.9	1.4	1.3	1.4	1.5	1.4	1.6	1.7
U	5.5	1.0	.93	.89	1.4	.95	1.1	1.1
Zr	74	1.3	1.4	1.3	1.6	1.6	2.1	1.6
Hf	2	1.4	1.6	1.5	1.7	1.7	1.8	1.8
V	34	1.4	1.8	1.3	1.7	1.8	2.6	1.1
Nb	7	1.3	1.3	1.5	1.5	1.6	1.7	1.6
Ta	.8	1.2	1.3	1.9	1.9	2.1	2.2	2.4
Cr	53.5	.72	.88	.91	1.23	1.46	1.47	1.60
Mo	5.5	.9	1.1	1.3	1.9	1.8	2.1	2.2
W	.8	2.2	2.8	—	—	—	—	—
Ir	—	—	—	—	—	—	—	—

The lime-rich oil-shale ashes are used as lime fertilizers in agriculture and replace lime in the chemical industry, as a binder to produce building materials besides high-grade cement, light-weight and normal autoclave concretes, slag wool, as well as in road construction [1].

The majority of low-grade coal and lignite ashes issue from quartz and clay minerals, owing accordingly restrained utilization potentiality, but sufficiently for complete use. The Central Electricity Generating Board (UK) recommends pulverized coal ash as the main raw material of the building and construction industry, where it is used as a structural fill, in block and light-weight aggregate manufacture, concrete and cement, ground stabilization and brickmaking, also as a filler in industries as diverse as refractories, paints, plastics, chemicals, filtration, insulation and fire protection [3, 4].

In cases of great variability of ash qualities, for example, by horizontal mining extraction of very thick coal deposits in open-pit mines in Germany, also peat utilization on power stations ash is applied mainly to recultivating mined-out areas.

Special uses are to the furnace-bottom slag from pulverized fuel liquid-bath furnaces, but on oil-shale combustion it is not ordinarily possible to have temperatures high enough for this type of furnace.

Fluidized Bed Combustion Ashes. Similarly to the pulverized fuel combustion, the fluidized bed combustion issues also two kinds of ash: bottom ash and fly-ash. But the material is coarser and the share of the furnace bottom ash is mostly predominating over the share of fly-ash.

In fluidized bed furnaces the temperatures are lower than in pulverized fuel furnaces. The longer retention period of mineral particles in the furnace usually does not compensate for the losses on reaction velocities of minerals by lower temperatures, especially concerning fly-ash. The laboratory experiments of H. Taal in 1964...1966 at temperatures 1300...1800 K have shown an exponential dependence of ash potassium volatilization velocity on the temperature demonstrated in [5].

In 1972...1983 some pulverized oil-shale fired boilers were reconstructed for low-temperature vortex burning and for fluidized bed combustion (torch-fluidized burning) with cooling panels in the active zone of the furnace. Coarse grinding of the fuel and the decrease in the temperature in the furnaces by 150...250 K has resulted in the decrease in intensity of fouling the boiler heat surfaces with ash deposits. The fly-ash utilization facilities are not investigated, but there is no doubt about the ash utilization as lime fertilizer.

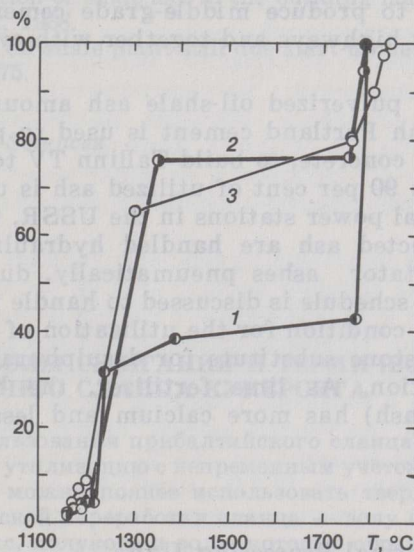


Fig. 2

Cumulative with temperature increase weight of liquid oil-shale fractions separated by density: 1 and 2 — oil-shale ground in 8 t/h wall mills: 1 — first stage rough grinding mill ($R_{60} = 69.6$ and $R_{200} = 46.6\%$) and 2 — final stage fine grinding mill ($R_{60} = 27.3$, $R_{90} = 11.4$ and $R_{200} = 1.3\%$); 3 — oil-shale ground in axial air-inlet hammer mill 1500/1181 ($R_{60} = 41.8$, $R_{90} = 20.2$ and $R_{200} = 1.7\%$)

The ground oil-shale is dispersed in separate particles with mineral matter content from 10 to 99 per cent, with calcium oxide content from 6 to 80 per cent and with ash melting point from 1165 to 1870 °C [6].

Figure 2 demonstrates how with a coarser grinding of oil shale the relative amount of low-temperature melting ash particles decreases [6, pp. 26—42]. The ground oil-shale separate particles have the ash melting points lower than 1300...1350 °C or higher than 1750 °C (clay

and sand minerals with low melting temperatures and carbonates with very high melting points) [6].

Whereas the furnace chamber maximum temperatures with boiler load fluctuating are variable between 1300...1500 °C, the variability of load does not have a substantial influence on the thermal treatment quality of pulverized oil-shale ash. But the temperatures on the low-temperature vortex or fluidized bed combustion of oil-shale, between 1100 and 1350 °C, are not sufficient to guarantee the stability of thermal treatment of the ash as a building material.

Selective Ash Separation and Utilization. The utilization of pulverized oil-shale ash is based on the selective ash separation in the boiler units, as well as on the relative stability of ash quality rates.

V. H. Kikas demonstrated [1, Fig. 1] the variability of pulverized oil-shale ashes, as well as the composition of separately handled parts. The stability of quality of the narrow-limited finest fly-ash fraction (particle sizes less than 15 micrometers to produce high-grade shale-ash Portland cement) is guaranteed by effective cyclone collector with the efficiency of about 60...70 per cent, installed before the electrostatic precipitator collecting this ash fraction. Fly-ash fraction with particle sizes below 30 micrometers is collected in electrostatic precipitators installed after inertial collectors with the efficiency of 15...40 per cent, protecting the fine ash from the intervention of coarser particles. This fine fraction is used to produce middle-grade cements, autoclave concretes, in constructing highways and together with cyclone ashes as lime fertilizer [1, 7].

The yearly utilized pulverized oil-shale ash amount in the USSR is nearly 4 million t. Ash Portland cement is used to produce responsible prestressed reinforced concrete, to build Tallinn TV tower, high chimney stacks, etc., but about 90 per cent of utilized ash is used as fertilizer.

At oil-shale electrical power stations in the USSR, the bottom ash and in the gas duct collected ash are handled hydraulically, cyclone and electrostatic precipitator ashes pneumatically, duplicated with hydraulic ash removal. A schedule is discussed to handle the bottom and gas duct ashes also in dry condition for the utilization of these ashes as lime fertilizer and as limestone substitute for desulphuration of flue gas at the same power station. As lime fertilizer, the bottom ash (about 40 per cent of total ash) has more calcium and less inadvisable trace elements (Table).

Solid Residues of Thermal Processing Units

There are diverse methods of thermal processing of oil shale for synfuels (liquid and gaseous).

The thermal processing temperatures (usually between 500 and 1000 °C) are not sufficient for optimum thermal treatment of solid residue. For example, the gas producer type retorts to lumpy oil shale processing with air-steam blast in the bottom section did not guarantee the ash residue suitable for use as a fertilizer or building material.

The main problem with solid residue at the thermal processing of low-grade fuels is not the ash utilization problem, but the problems of harmless depositing of the processed fuel preventing the transfer of water-soluble salts and various compounds of incomplete oxidation by surface runoff waters into open water reservoirs.

The problems of processed fuel disposals have not been solved. The processed shale disposal of Union Oil plant in Colorado is a dry-bottom canyon where it is spread, compacted, contoured and revegetated.

Disposal and recovery of saline percolate and runoff waters is designed. Studies are under way to monitor water migration [8].

In Estonia, for the new Kiviter oil-shale processing plant a hydraulic processed-shale disposal is designed. Whether the pulverized oil-shale ash concrete disposal area bottom cover and walls are sufficiently water-impervious is a problem.

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ИСПОЛЬЗОВАНИЕ ЗОЛЫ СЖИГАНИЯ И ТЕРМИЧЕСКОЙ ПЕРЕРАБОТКИ ЭСТОНСКОГО ГОРЮЧЕГО СЛАНЦА-КУКЕРСИТА

Рациональность использования прибалтийского сланца-кукерсита подразумевает его комплексную утилизацию с неизменным учетом экологических аспектов. Необходимо как можно полнее использовать твердый остаток энергетической и технологической переработки сланца — золу его сжигания в котлах электростанций и кокс, полукокс и золу, которые образуются при полукоксовании кукерсита в сланцевых генераторах. В последнем случае очень важно, чтобы складываемые в золных отвалах остатки переработки не наносили ущерба окружающей среде.

Зола сжигания полностью окислена и имеет широкую сферу применения: в сельском хозяйстве в качестве удобрения и для известкования почв, в промышленности строительных материалов для получения высококачественных цементов и тяжелых автоклавных бетонов, кирпича и теплоизоляционных материалов, в дорожном строительстве в качестве вяжущего, в химической промышленности и т. д.

Качество сланцевой золы, а следовательно, и эффективность ее использования во многом определяется методами сжигания и термической переработки, а также способами газоочистки и золоудаления. В этом плане весьма перспективно селективное осаждение золы в многоступенчатых фильтрах.

Академия наук Эстонии