Oil Shale, Vol. 12, No. 4
pp. 357-361

ISSN 0208-198X

UTILIZATION OF SHALE PROCESSING WASTES IN THE CEMENT INDUSTRY

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This article describes the results of an investigation into the use of shale ash as a raw mix component in cement manufacture. The ash is a waste product from the SHC-3000 unit which processes shale fines with a solid heat carrier.

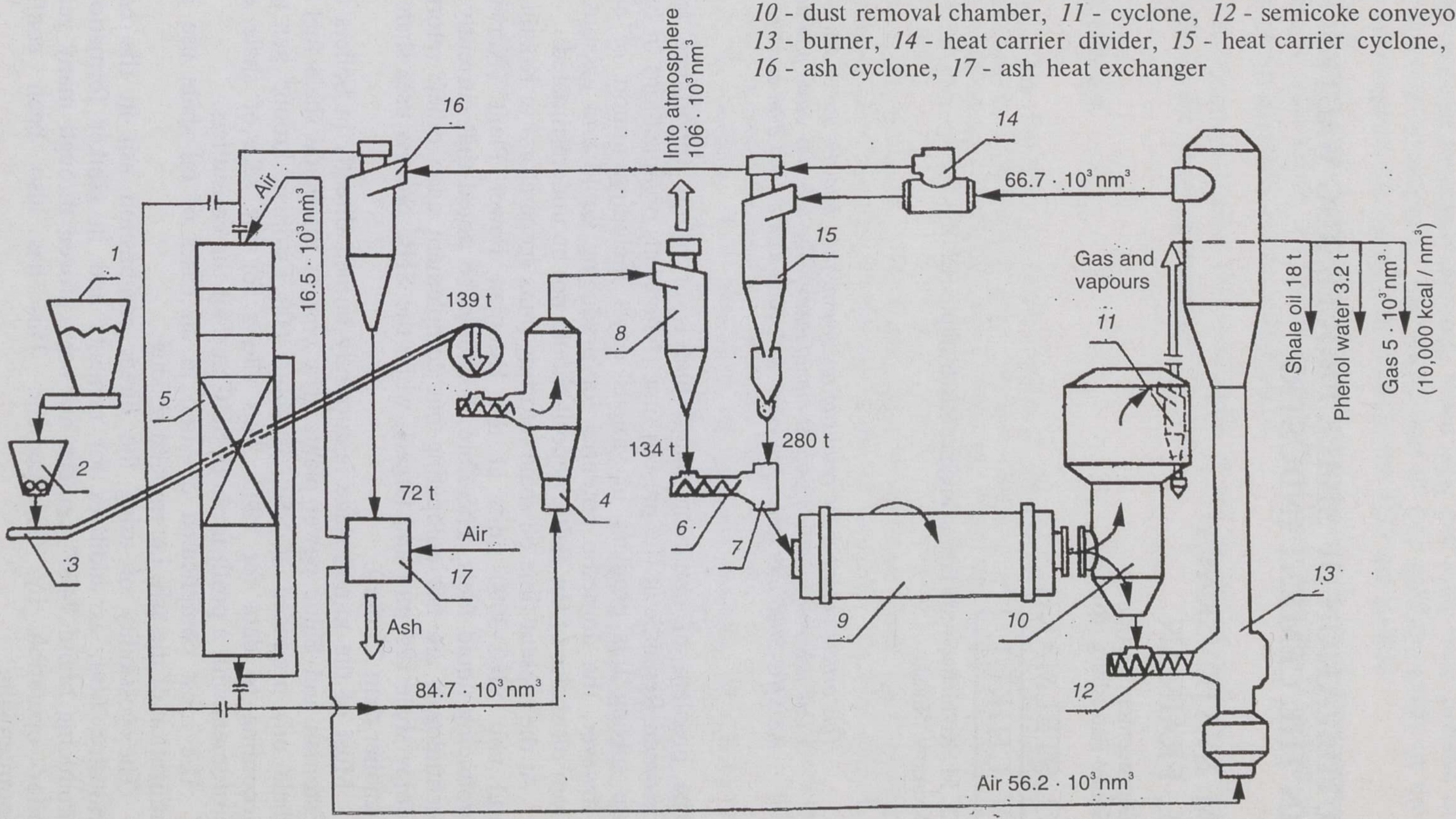
The problem of obtaining liquid fuel is of prime importance for the Estonian Republic at the present time. Numerous organizations in Estonia are solving this problem in various ways, including import of energy. However, the domestic potential for producing liquid and gaseous fuels from oil shales of the Baltic deposit should not be underestimated.

At the present time oil shale retorting units (generators) in Kohtla-Järve and two SHC-3000 units at the Estonian Power Plant (Narva) are producing liquid fuels. Therefore, it should be noted that currently these technologies are not competing but complement each other: retorts use lumpy shale (25 mm and larger), while the SHC process uses shale fines (smaller than 25 mm).

Most of the mined shale is currently burned directly in boilers at the Estonian and Baltic power plants. The cost of the liquid shale fuel (total shale oil) produced at SHC is about 600 Estonian kroons per tonne, according to data for 1993. This allows for the sale of shale oil to customers with a profit for both SHC and for the consumers.

The most complicated question in all cases of oil shale use is the utilization of the ash, i.e. mineral residue.

The possibility of using the direct combustion ash in the cement industry, both as additives for cements and in clinker formation for producing brand "400" cement has been proved through many years of prior operation by Giprocement. This has also been confirmed commercially.



SHC-3000 process flowsheet: *1* - bin, *2* - crusher, *3* - feed shale conveyor, *4* - drier, *5* - waste heat boiler, *6* - dry shale conveyor, *7* - mixer, *8* - dry shale separator, *9* - rotary drum reactor, *10* - dust removal chamber, *11* - cyclone, *12* - semicoke conveyor, *13* - burner, *14* - heat carrier divider, *15* - heat carrier cyclone, *16* - ash cyclone, *17* - ash heat exchanger

The ash from the SHC-500 and SHC-3000 units were also studied by Giprocement with the same objective. On the basis of these studies it was concluded that the SHC ash formed during shale fines processing can serve as a raw material for the cement industry.

These results concern not only Estonian oil shale ashes but also those of north-west of Russia as well as of other countries, e.g. Israel.

The SHC-3000 units now operate quite effectively at the Estonian Power Plant and have some advantages over the similar American process: TOSCO-2. The TOSCO-2 process uses special 0.5-inch ceramic balls as a solid heat carrier in contrast to the ash used in the SHC-3000 unit. The TOSCO-2 process plant has a complicated system requiring process units for solid heat carrier separation, transport, etc. An additional important fact is that currently there are no other commercial plants in the world which process shale fines on the scale of the SHC-3000 unit. The demonstration plant based on the TOSCO flowsheet of 900 ton-per-day of shale throughput operated about a year and was shut down several years ago.

The SHC-3000 unit (pyrite department) is shown in Figure [1]. The design hourly flow rates are presented in it. These rates differ very little from the actual rates in the plant.

Oil shale from Bin *1* is crushed in Crusher *2* to a maximum lump size of 25 mm. The lump shale is then supplied by Conveyor *3* to Drier *4* where flue gas, with a temperature of about 600 °C from a Waste Heat Boiler *5*, is also fed in. The dried shale, which is warmed up to 110-150 °C in the Drier, enters through Dry Shale Separator 8 and Dry Shale Conveyor 6 into Mixer 7. Mixer 7 also receives the heat-carrier ash which is at a temperature of 780-800 °C when it is delivered from Cyclone *15*. The flue gas from the Drier, after shale dust separation in Separator *8*, is vented to the chimney stack. The mixture of shale and heat-carrier ash from the Mixer enters Rotary Drum Reactor *9*.

As a result of interaction with the heat carrier, the shale is heated up to a temperature of 470-500 °C, and a gas-vapour mixture is formed in the Reactor. Then the mixture and spent shale are directed to the Dust Removal Chamber *10* where the suspended particles are removed from the mixture as a result of low velocities. Additional particle removal is effected in special Cyclones *11*. After cleaning, the gas-vapour mixture is directed to the condensation unit.

The organic matter which was not gasified in the Reactor, together with the mineral part of the fuel, is supplied by Semicoke Conveyor *12* to the Burner *13*. There it is finally burned in the air flow. The combustion products formed in the Burner (temperature 780-800 °C) are directed (after Divider *14)* partly to Heat Carrier Cyclone *15* and partly to Ash Cyclone *16,* where ash is removed. The ash collected by Cyclone *15* serves as a heat carrier for shale heating and is directed to the mixer. The ash collected by Cyclone *16* is removed from the cycle after cooling in the Ash Heat Exchanger *17*.

The high-temperature combustion products, which are separated from the ash in the cyclones, are discharged to the Waste Heat Boiler for use as a fuel. The semi-coke gas from the condensation unit is also supplied to the Waste Heat Boiler for combustion. The Waste Heat Boiler provides on-site steam and electric power requirements.

The dry ash from the ash heat exchanger of SHC-3000 has characteristics which allow its use in the cement industry. The detailed study of the ash residue composition showed that it is specific in both principal chemical component (SiO_2, CaO, Fe_2O_3) and minor oxide (SO_3, K_2O, Cl) content. The average composition of the ash residue obtained at the SHC-3000 units is given in Table. Its specific composition, along with the occurrence of unburned fuel particles, determines the acceptability of the residue as a cement mix feed component.

Table 1. **Ash Composition**

Indices	Processing temperature	
	850 °C	730 °C
Content of components, % mass:		
SiO_2	22.5	16.1
Al_2O_3	3.9	3.0
Fe_2O_3	4.06	3.90
CaO	40.6	39.0
MgO	1.9	3.6
SO_3 total	8.5	5.0
K_2O	2.5	2.2
Na_2O	0.1	0.1
Cl	0.3	0.2
CaO free	7.8	1.3
LOI, % mass	14.0	27.7
Real composition:		
Calcite	55	80
Anhydrite	5	7
Quartz, feldspars	20	13
Others	20	–

The calculated compositions of the cement feed mixture determine the possibility of obtaining clinker with the proper composition using a two-component mix, i.e. shale ash and limestone. Normally, the quantity of limestone necessary for achieving the required module characteristics of the feed mixture ($KH = 0.92$; $n = 2.3$; $p = 1.4$) will not exceed 20 %.

A comparative thermal analysis of mineral formation with a conventional feed mixture and a mixture using oil shale ash indicates the following effects with the shale ash mixture: (1) an endothermal effect occurs at about 480 °C, which is indicative of the presence of kerogen, (2) some displacement of the decarbonation effect to the low-temperature zone, and (3) a marked intensification of the mineral formation process in the high-temperature zone.

The distinguishing feature of the feed mixtures prepared by using oil shale ash is their high content of magnesium oxides, alkali metals, and sulfuric anhydride. Phosphoric anhydride is also present in amounts exceeding 1.5 %.

The set of factors mentioned above severely complicates the problem of producing a high-quality clinker with the utilized components. At the same time, experiments carried out at the Giprocement pilot plant showed that the phase composition of the produced clinkers have a number of unique features. These tests burned a feed mixture prepared from shale ash obtained from the SHC-3000 unit operated with a 50 % recycle.

These cements are characterized by a shorter induction period as compared to traditional feed mixtures.

Physical and chemical methods enable one to record an appreciable increase in the content of the alite phase (up to 10 %) and the aluminate component (up to 20 %) as compared to the half-finished product of conventional composition.

The features mentioned above result from exceptionally favourable conditions generated by the components present during the mineral formation process.

Cements produced on the basis of the compositions under study (when ground to 8 % residue on a No. 008 sieve) were characterized by a more rapid strength gain during the early hardening period (3 days) and high 28-day strengths.

The results of our experiments allow one to draw the conclusion that, aside from the tackling of an important ecological problem through utilization of the ash residues obtained from decomposition of oil shale in SHC-3000, and aside from a considerable power saving (more than 6 %), there is apparently a possibility of producing high-quality clinkers and cements from ash-based feed mixtures due to specific features of this raw material. Production of cements with a special set of properties is feasible through the use of the studied waste material.

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Presented by V. Proskuryakov
Received July 25, 1994