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COMBINED UTILIZATION OF OIL SHALE ENERGY AND OIL SHALE MINERALS WITHIN THE PRODUCTION OF CEMENT AND OTHER HYDRAULIC BINDERS

J. HILGER*

Rohrbach Zement
Dormettinger Str. 25, D-72359
Dotternhausen, Germany

In Dotternhausen, Germany, Rohrbach Zement has been successfully using Posidonia shale in a complex process for more than 60 years. The oil shale is rather poor with only 9 % organic matter, a calorific value of 3400 kJ/kg, an oil yield of 40–45 l/t and an ash content of 71 %. The deposit consists of a 9-m-thick flat layer of bituminous calcareous marl, which is mined in an open cast mine. The utilization of oil shale is integrated into the manufacture of cement and other hydraulic binding agents. Part of the oil shale is directly used in the precalciner of the rotary kiln for cement clinker production. Finely ground oil shale supplies 20 % of the thermal energy and 10 % of the raw minerals needed for the clinker burning process. Most of the oil shale however is burnt at certain conditions in fluidized-bed units to produce burnt oil shale with remarkable hydraulic properties. The heat of this burning process is used simultaneously to produce electricity. Hydraulic burnt oil shale is mainly used together with clinker to make Portland-Burnt Shale Cement (CEM II/B-T), according to European standard EN 197-1. But it is also suitable to produce burnt shale based binding agents for many applications in civil and soil engineering. The profitability of this oil shale operation is based on the complete utilization of both the oil shale energy and all of its minerals.

Oil Shale in Dotternhausen

In Germany oil shale was deposited in the Toarcian Age, 180 million years ago, in a shallow sea. The deposit today is deeply buried in northern Germany and serves as a source rock for the oil and gas fields of the north sea. In Baden-Württemberg in south-west Germany the oil shale is exposed at the surface in the area between Stuttgart and Lake Constance. The name of this oil shale is Lias ε or Posidonia shale.

* e-mail: *juergen.hilger@rohrbach-zement.de*

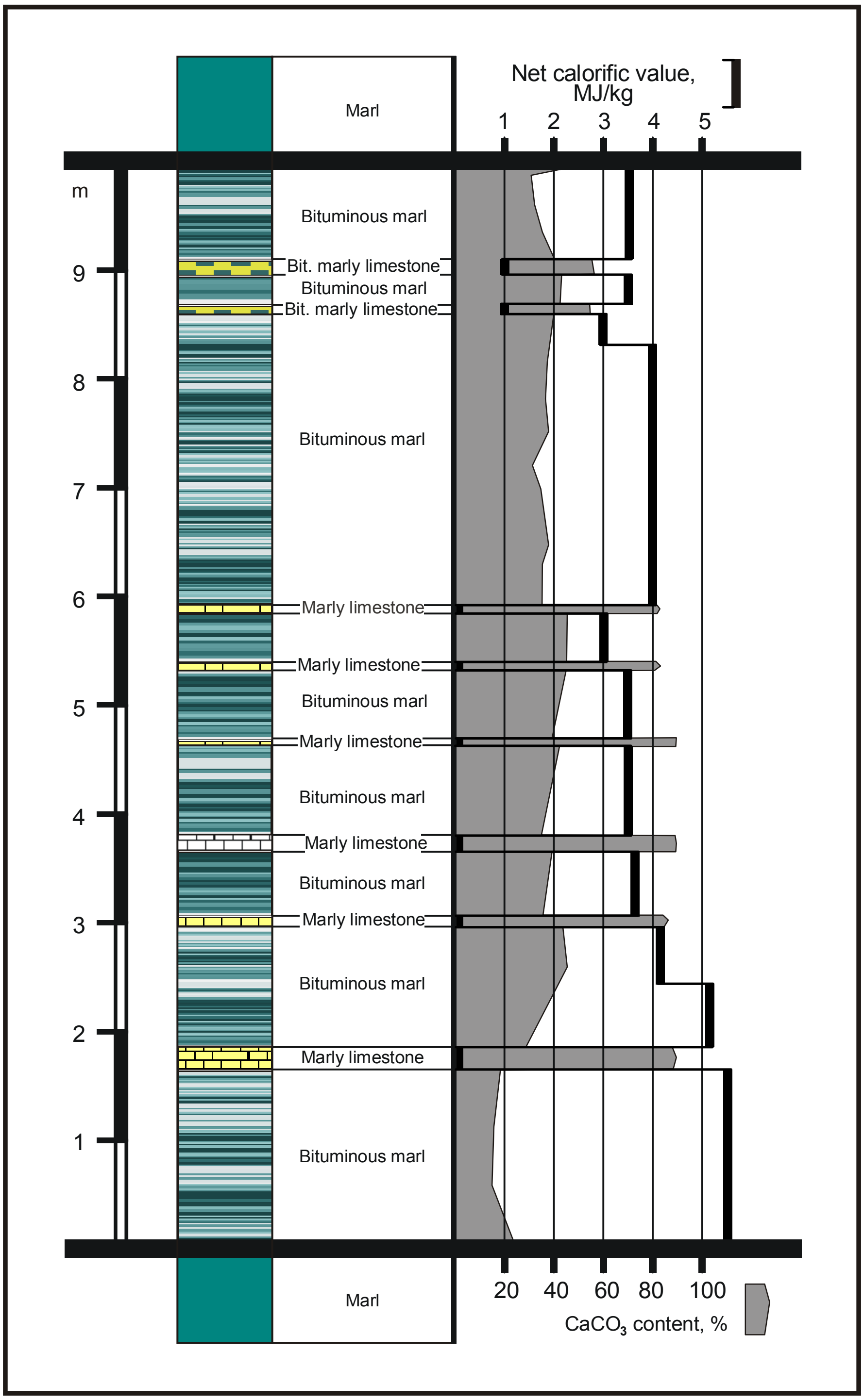

Fig. 1. Geologic section of the Dotternhausen oil shale deposit showing the variation in $CaCO_3$ content and net calorific value

In Dotternhausen, the place of Rohrbach Zement's oil shale operation, the oil shale deposit has a thickness of 9 meters. It is flatly layered, tectonically rather undisturbed and covered by only 1 or 2 meters of waste.

The deposit is rather homogeneous in the lateral extension but the vertical section shows different qualities. The rock can be described as a bituminous marl containing some intercalations of limestone. Figure 1 shows the section of the oil shale giving the $CaCO_3$ content and the net calorific value of the individual layers.

The petrographic analysis and the chemical analysis are given in Table 1. The major part of the oil shale is calcium carbonate besides clay minerals and some quartz. The hydrocarbon content is about 9 %. Hydrocarbons and the CO_2 from the carbonates together give a loss on ignition of 29 %. The sulfur content of 2.8 % is of great relevancy for the utilization of the oil shale minerals.

Table 1. **Chemical and Petrographic Analysis of the Dotternhausen Oil Shale**

Chemical analysis	
Hydrocarbons	8.8 %
CO_2	20.2 %
SiO_2	25.1 %
CaO	23.9 %
Al_2O_3	10.4 %
Fe_2O_3	4.7 %
S	2.8 %
MgO	1.3 %
Others	2.8 %

Petrographic analysis	
Hydrocarbons	8.8 %
Calcium carbonate ($CaCO_3$)	42.7 %
Clay minerals (especially illit and kaolinit)	28.8 %
Quartz (SiO_2)	11.8 %
Pyrite (FeS_2)	4.0 %
Others	3.9 %

The most important properties of the Dotternhausen oil shale are:

- a lower calorific value of 3400 kJ/kg
- an oil yield of 40–45 l/t
- an ash content of 71 %
- and a calcium-rich mineral content

With these properties it is obvious that a utilization of only the oil shale energy cannot be economical. The energy content and the oil yield are too low and the amount of residues or ashes is too large.

A breakthrough was reached in the 1930s, when Rudolf Rohrbach found out that it is possible to burn the oil shale in a way that it develops hydraulic or cementitious properties. That means that the burnt shale, when mixed with water, gets hard and develops strength like cement. The consequence of this finding was the development of a process that integrates the utilization of oil shale into the process for manufacture of cement and that makes use of all the oil shale energy as well as of all its minerals.

Dotternhausen was chosen for this operation because at this location all the raw materials that are needed for an oil shale cement plant are available in the vicinity (Fig. 2). All the sediment strata of the Jurassic Age are exposed on the edge of the Swabian Alb. Limestone, the major raw material for cement manufacture, is mined from the Malm strata at an elevation of 1000 m above sea level. Clay is mined from the Dogger strata below the limestone. Oil shale is found in the direct vicinity of the cement works; in fact the plant was built on the oil shale deposit.

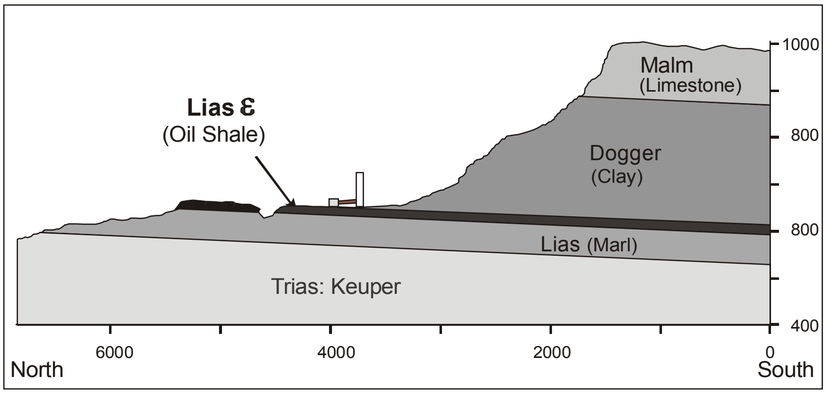

Fig. 2. Jurassic strata exposed at the edge of the Swabian Alb

Two Process Lines

Process technology has changed through the decades but all the time oil shale was used as an energy source and as a mineral raw material. Today there are two process lines, in which oil shale is utilized:

1) The rotary kiln for manufacture of cement clinker.
2) Three fluidized-bed units for manufacture of hydraulic burnt shale and for generation of electric energy.

To produce cement clinker in a **rotary kiln** one needs mineral raw material and energy. Both can be supplied by oil shale. The necessary specific heat for clinker production is about 3200 kJ per kg clinker. The composition of the raw material has to correspond exactly with the composition of the clinker to be produced, especially the elements CaO, SiO_2, Al_2O_3 and Fe_2O_3.

The ground raw material is fed into the top of the preheater tower (Fig. 3). It passes through the stages of cyclones, where it is heated by the counterflow of hot gas. Before entering the kiln tube raw material reaches the precalciner where, at a temperature of about 800 °C, the carbonates are dissociated. To achieve this temperature and to supply the dissociation heat, fuel is needed in the precalciner. In the rotary kiln the minerals are then further heated to 1450 °C, the temperature at which the desired clinker minerals form. This section of the kiln is fueled from the primary burner at the outlet end of the kiln tube.

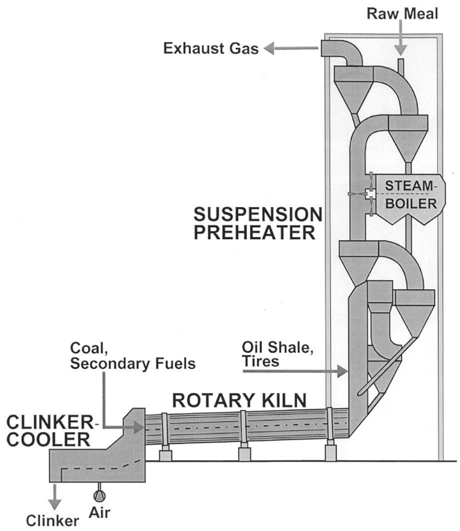

Fig. 3. Rotary kiln with suspension preheater for clinker production with the use of oil shale

In this process oil shale can well be used in the precalciner because fuel is needed here, and the oil shale minerals can easily participate in the chemical reactions in the rotary kiln. Preconditions are: the oil shale has to be ground to 14 % <90 µm and its mineral composition must fit into the raw mix.

With these materials we find a mix which contains about 10 % of the mineral part of the oil shale. The mix supplies the reactants in the correct proportion to form the clinker minerals (Table 2).

Table 2. **Mineral Raw Material for the Rotary Kiln, the Reactants and the Final Clinker Minerals**

Mineral Raw Materials			**Reactants in the Rotary Kiln**			**Clinker**	
Limestone	80.1 %						
Oil shale (mineral part)	9.7 %	→	CaO (*C*)	65.1 %	→	C_3S	52.7 %
			SiO_2 (*S*)	19.8 %		C_2S	17.1 %
Clay	6.7 %		Al_2O_3 (*A*)	6.3 %		C_3A	11.7 %
Sand	2.8 %		Fe_2O_3 (*F*)	3.0 %		C_4AF	9.2 %
Hard coal (mineral part)	0.7 %						

Summarizing the utilization of oil shale in this process one can say that oil shale supplies 20 % of the fuel heat and 10 % of the mineral raw material to clinker production in the rotary kiln.

The major part of the mined oil shale, more than 80 %, is burnt in **fluidized-bed units**. Two units were built in 1963, a third one in 2001. Oil shale with a grain size of 0–10 mm is continuously fed to the fluidized bed at a rate of 16 t/h for each unit (Fig. 4). Air enters the unit from the bottom through a grate to fluidize the material and to supply the oxygen for combustion. The fluidized bed is stationary, contrary to circulating fluidized beds that have also been applied for oil shale in other countries. Combustion is controlled at a temperature of 800 °C. This is the optimum temperature to achieve the best properties of the burnt shale, that means especially the maximum strength.

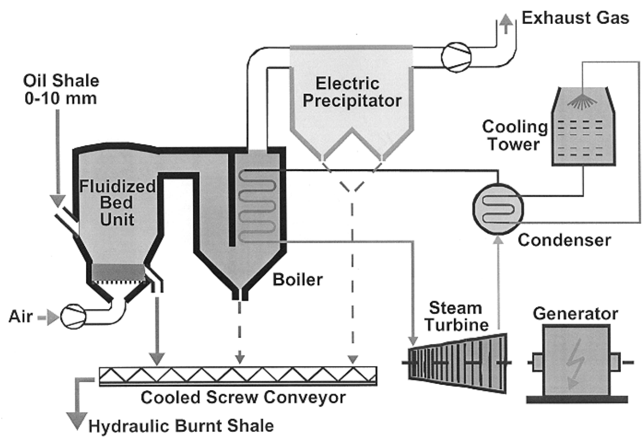

Fig. 4. Fluidized-bed unit for the production of hydraulic burnt shale and electric energy

The sulfur which escapes during burning is completely absorbed by the lime of the shale. It gives the burnt shale an SO_3 content of 10 %. The burnt shale, after leaving the fluidized bed, is cooled and stored in silos.

The hot gas from the fluidized-bed unit is used in a steam boiler to produce superheated steam before it is cleaned in an electrostatic precipitator and leaves through the stack. The steam has a temperature of 490 °C and a pressure of 59 bar. The steam from the three units is converted in two turbo sets to 11.2 MW electric power. This is more than the average consumption of the cement works. The company is connected to the public supply network which makes it possible to exchange electricity. In the balance the plant is a supplier of electricity.

Summarizing this process line shows that one process yields two products (Fig. 5). From 1 t of oil shale 0.71 t of hydraulic burnt shale as a valuable intermediate product for cement and binder production is formed. Additionally 270 kWh electricity is generated, which exceeds the own requirements.

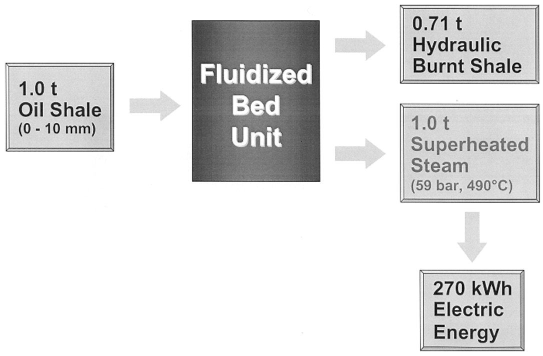

Fig. 5. One process (fluidized-bed unit) – two products (hydraulic burnt shale + electric energy)

High-Quality Mineral Products

The quality of the burnt shale from the fluidized-bed units corresponds to the European cement standard EN 197-1. The requirements for burnt shale as a component of cement are defined in the standard. The hydraulic and pozzolanic properties of the burnt shale must give a strength of minimum 25 MPa after 28 days. The Dotternhausen burnt shale reaches a compressive strength of 35 MPa after 28 days! The conformity with the standard allows the burnt shale to be used for manufacture of standard cement.

Main product of Rohrbach Zement is Portland-burnt shale cement CEM II/B-T in the strength classes 32.5, 42.5 and 52.5 (Fig. 6). This is a cement of high quality which competes with ordinary Portland cement and other composite cements. It can be used in any type of concrete, either ready mixed or prefabricated. Strength development is usually slightly different from ordinary Portland cement: lower at the beginning and higher at the end. But even this can be adjusted by the advanced technology of a new cement-grinding plant, which was commissioned in 2002.

EN 197-1		Main constituents, %				Minor add. const., %
		Clinker	…	Burnt shale	…	
Portland-Burnt Shale Cement	CEM II/A-T	80-94	–	6-20	–	0-5
	CEM II/B-T	65-79	–	21-35	–	0-5

Fig. 6. Portland-Bunt Shale Cement in the European cement standard

The amount of burnt shale in the cement is limited by the 35 % of the standard or by the SO_3 content of the cement, which is limited to 4.5 %. The high sulfate content of the burnt shale is used to adjust the setting time of the concrete. No additional sulfate, such as gypsum or anhydrite, is needed.

It is the cement mill where the two process lines come together: clinker from the rotary kiln and burnt shale from the fluidized-bed units meet in the cement mill to be ground to Portland-burnt shale cement. Since burnt shale has been moderately burnt from a soft rock and has become porous by the loss on ignition it is very easy to grind. The specific grinding energy of cement containing 27 % of burnt shale is 50 % lower than the grinding energy of an equivalent Portland cement. This also adds to the efficiency of an oil shale cement works.

Portland-burnt shale cement is not the only product based on oil shale. Burnt shale with its very special properties is a material that serves as a basis for a new generation of cementitious binding agents. It is the very high fineness of burnt shale, 8,000–10,000 cm^2/g according to Blaine, and its cementitious properties that qualify this material for many applications in the building market and in civil engineering.

Rohrbach Zement has developed a large number of burnt-shale-based products for civil and soil engineering, which are distributed by its subsidiary Georoc.

Here are some examples:

- Injections of soil and rock e.g. to shore up foundations in soft ground or in tunneling.
- Stabilization and melioration of clayey soil e.g. in road building or for embankment; also available for dust-free application.
- Filling of underground cavities and sewers that are no longer used and have to be prevented from caving in.
- Sealing by subterraneous curtains or by injection e.g. to keep groundwater out of an excavation.
- Stabilization and solidification of sludge dumps or mud settling ponds e.g. of sewage sludge or industrial waste sludge.
- Immobilization of pollutants in contaminated soil e.g. of old industrial sites.

Summary

The key to success with this low-calorific oil shale is the entire utilization of the energy and the minerals. This is consequently done in two separate process lines (Fig. 7). In the rotary kiln for clinker production oil shale supplies part of the fuel heat and part of the mineral raw material. In three fluidized-bed units oil shale is burnt to form a cementitious binding agent. The heat from this process is used to generate electricity, more than the cement works own demand. Clinker from the rotary kiln and burnt shale from the fluidized-bed units are used to produce Portland-burnt shale cement and cementitious binding agents for civil and soil engineering.

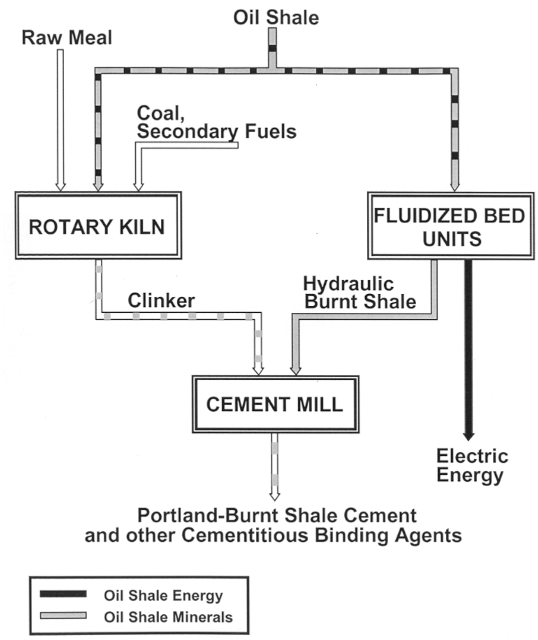

Fig. 7. Combined utilization of oil shale energy and oil shale minerals at Rohrbach's cement works

This way oil shale supplies 52 % of the cement works total energy consumption. Looking at the electrical energy only, it is more than 100 %. A part of 38 % of the mineral products of the cement works, that is more than one third, is formed by oil shale minerals.

Rohrbach Zement in Dotternhausen has in fact favorable conditions for this kind of operation: the calcium-rich oil shale, the proximity of all raw materials, the infrastructure and the market. Probably there is a potential for combined oil shale utilization at many deposits in the world. The calcium content of the oil shale is not necessarily a criteria. There are calcium-rich oil shales in the world that are likely to form hydraulic binding agents. The silicium-rich oil shales can, however, also be used in cementitious binder production because of their pozzolanic properties.

Whatever one does with oil shale or whatever one is planning to do with oil shale, the combined utilization of the energy and at least of a part of the minerals will increase the profit of the operation.