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Characterization of raw and burnt oil shale from Dotternhausen: Petrographical and mineralogical evolution with temperature

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ABSTRACT

The Toarcian Posidonia shale from Dotternhausen, Germany, is quarried and burnt in a fluidized bed reactor to produce electricity. The combustion residue, namely burnt oil shale (BOS), is used in the adjacent cement work as an additive in blended cements. The starting material is a typical laminated oil shale with an organic matter content ranging from 6 to 18%. Mineral matter consists principally of quartz, feldspar, pyrite and clays. After calcination in the range, the resulting product, burnt oil shale, keeps the macroscopic layered texture however with different mineralogy (anhydrite, lime, iron oxides) and the formation of an amorphous phase. This one, studied under STEM, reveals a typical texture of incipient partial melting due to a long retention time (ca. 30 min) and quenching. An *in-situ* high temperature X-ray diffraction (HTXRD) allowed studying precisely the mineralogical changes associated with the temperature increase.

1. Introduction

Although oil shale has been calcined to benefit from the pozzolanic properties of its ashes [1], burnt oil shale is generally a by-product from the oil shale industry, generated in huge amounts, especially in Estonia, Russia… [2]. Burnt oil shale is used in blended cements [3–6], in brick manufacture [7], attempts have been made in order to use it in ceramics [8] or to hydrate them as "oil shale stone" [9]; when not valorized it is simply landfilled [10].

The present study reviews a specific oil shale/burnt oil shale tandem from southern Germany, where a Posidonia shale is quarried and burnt in a fluidized-bed reactor which supplies an adjacent cement plant with electricity. The specificity lies in the uniqueness of the industrial process, in which the shale is used both raw for clinker production and burnt as an additive in blended cements (Fig. 2, see also http://www.holcim.com/referenceprojects/greater-building-sustainability-with-holcim-optimo.html). According to Taulbee et al. [11], "*The Rohrbach cement works* (author's note: now Holcim since 2003) *in Dotternhausen, Germany, is one of the more tightly controlled and technically advanced cement plants in the world*". This site is active since 1939.

This study presents the characterization of both raw and burnt oil shale based on petrographic studies (optical microscopy, scanning electron microscopy coupled with energy dispersive spectrometry, scanning transmission electronic microscopy coupled with energy dispersive spectrometry), mineralogy (X-ray diffraction) and will review and summarize mineral evolution with temperature.

2. Materials and methods

Both raw and burnt oil shale come from the Dotternhausen cement plant in Germany, 70 km to the south-west of Stuttgart, and were provided by Holcim Süddeutschland. More precisely, the industrial site is divided in two parts: a cement plant s.s. with a rotary kiln and an electric power plant, generating steam, electricity and hydraulic binder [12]. The fuel for the power plant is an oil shale; the residue is burnt oil shale, used in the cement process to design composite cements (Fig. 1). Both raw and burnt oil shale is the material of the present study. In the fluidized bed reactor, the material divides into fly and bottom ashes [13]. Fly ashes (ca. 25% of the material), having a granulometry which does not exceed 250 μm, reach temperatures up to 980 °C, while the remaining ca. 75%, namely the bottom ashes, reaches only 980 °C. However, a distinction must be made between bottom/fly ashes and their granulometry: bottom ashes also contain fine particles. Historically, oil shale from this specific locality has drawn a lot of attention thanks to its use, and thus its valorization, in composite cements [14–20].

For the petrographic study, the Posidonia shale thin sections were made in a classical way according to the procedures described in Humphries [21].

A special care was taken for the preparation of burnt oil shale samples because of their extremely brittle nature. The samples were cast in epoxy resin; prior to vacuum impregnation, the samples were kept for at least 24 h in an oven at 40 °C. They were subsequently put in silicon molds and left in the vacuum impregnator 2 h before the resin was

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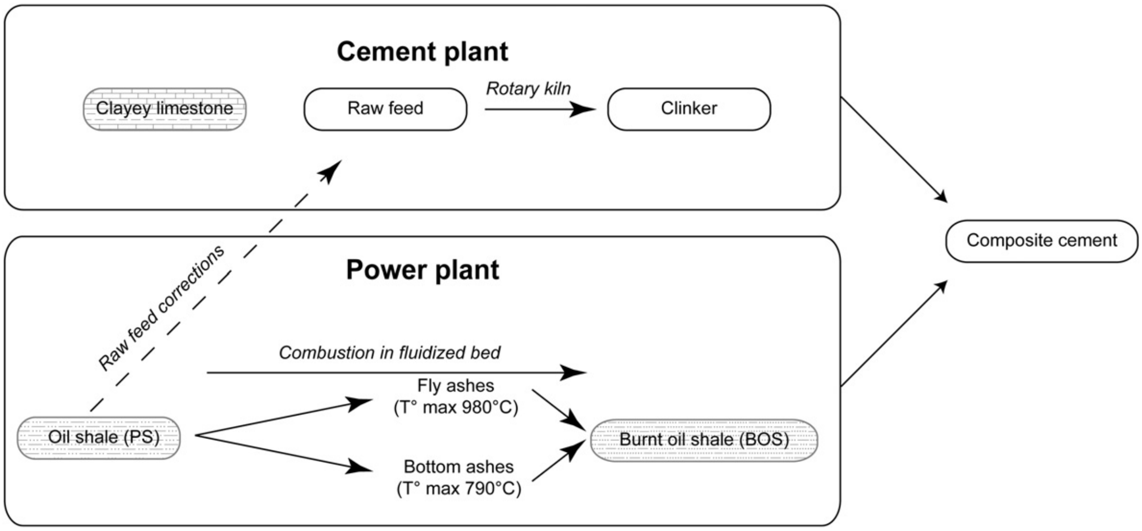

Fig. 1. The industrial process taking place in Dotternhausen.

cast. A special care was taken to avoid water contamination during thin section preparation; after sawing to a thickness of 100–150 μm, the thin sections were made by hand on a 500 grit *SiC* paper disposed on a glass plate until they reached a thickness of 20–30 μm, and they were then gently polished manually using 1200, 2400 and 4000 grit *SiC* papers disposed on a glass plate, using ethanol as a lubricant.

Scanning electron microscopy (SEM) imaging and analyses were carried out on a Hitachi S-4300SE/N SEM equipped with a Thermo Scientific Ultradry EDX detector. XRD analyses were carried out on a Bruker D8 advance equipped with a Co anticathode and a Lynxeye detector. Scanning transmission electronic microscopy (STEM), coupled with EDX, was performed on a FEI Tecnai G2 20.

High-temperature X-ray diffraction (HTXRD) was carried out using a D8 advance from Bruker (copper anticathode) operating in 2θ mode with the sample deposited on a platinum strip, acting both as sample holder and heating device. Each measurement was done from 7° to 52° (2θ) with a step size of 0,02°, counting time 1,6 s/step in order for each temperature step to last one hour. The heating rate between two temperature steps was of 5°C/s during both heating and cooling, excepted the last one (return to ambient temperature) with a 1 °C/ scooling rate. The atmosphere in the temperature chamber was air, injected with an 8 l/h flux. The successive temperature steps were carried out as follows: room temperature, then 100 °C and one temperature step every 100° until 900 °C, then 700 °C, 400 °C and room temperature.

3. Raw material: the Posidonia shale (or Posidonienschiefer), PS

The Posidonia shale is a lower Toarcian (also known as Lias ε) black shale. It is a widely studied formation from both paleontological, sedimentological and paleoenvironmental points of view [see review in

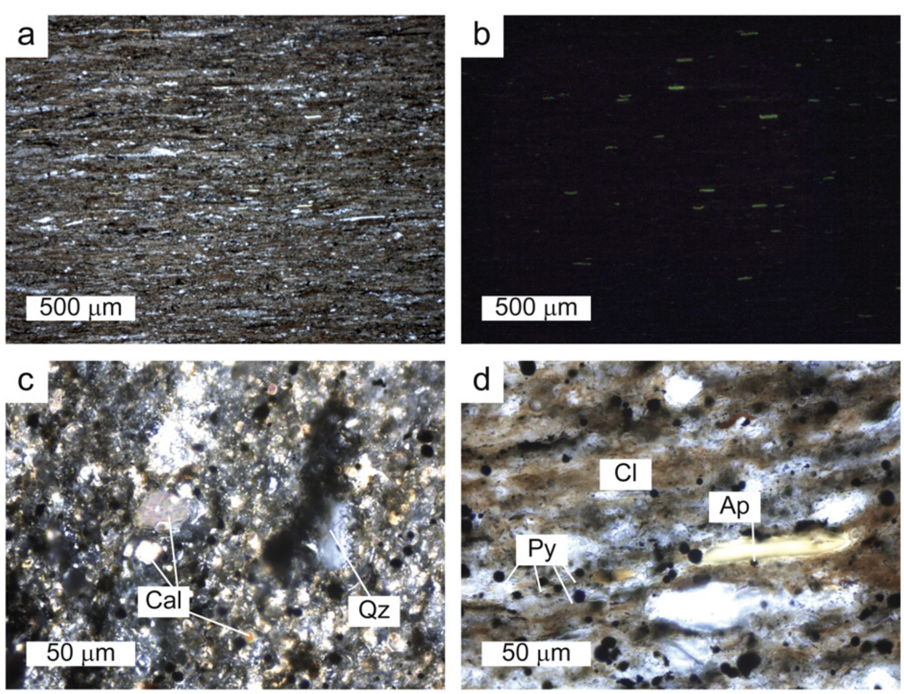

Fig. 2. a) Typical laminated Posidonia shale, transmitted light, uncrossed polars; b) same field of view as in a) seen under UV light to highlight the location of organic matter (mainly Tasmanales algae); c) calcite (Cal) and quartz (Qz); d) Richness in pyrite (Py- rounded opaque grains) throughout the laminated clay-rich (Cl) matrix, with apatite (Ap). Transmitted light, uncrossed polars.