A CONTRIBUTION TO THE CHARACTERIZATION OF THE „EISENBERGER KLEBSAND", SO CALLED "LUTING SAND", AS AN ECONOMIC RESOURCE AND A SUSTAINABLE RAW MATERIAL FOR REFRACTORIES

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ABSTRACT

With its impressive mineralogical description and its specific diversity, the unique alumosilicate raw material "Eisenberger Klebsand" attractive, technically-economic potentials to the development of innovative refractory products, that corresponds to the demand of a sustainable raw material-supply not least. The reliable availability of the natural alumosilicate raw materials of the "Eisenberger Klebsand" stands on that occasion in the context by the present, internationally tense supply-situation of ceramic raw materials currently, exemplary demonstrates by statistical evaluations of the "Association of the German Refractory Industry", original marks as "Verband der Deutschen Feuerfest-Industrie e.V. (VDFFI)" [1]. In order to become just for the demand of a sustainable and environment-amicable refractory production, a new objective were formulated in the framework of different current studies. Under application of advanced procedure-technologies specific raw material fractions of the unique alumosilicate in combination with selected carbon-sources and carbonaceous agents were transferred into composites. The well defined composites are able to be associated to the development and integrated into the production of silicate-ceramic construction-materials with maximum service temperatures up to 1550 °C. Granulate which include micro- and submicro-scaled alumosilicates showed technologically realizable application-qualities. Not least, the application of different variations of the composite material opens possibilities to join the native and long-term available raw material "Eisenberger Klebsand" with new technologies under economic and ecological points of view. As stood out until now, the technical application of the alumosilicate "Eisenberger Klebsand" faces a wide industrial application-potential within metallurgic technologies.

INTRODUCTION

Aim, function and demands

As part as well as former than also current studies, the rising demands on sustainable and environmentally compatible production of refractories were translated into an objective to integrate the specific silicate-ceramic raw material fractions of the „Eisenberger Klebsand", per definition named as luting sand (or loomy clay), well known in Europe as many decades [2], in combination with selected carbonaceous agents based on recent synthetic, environmentally friendly material and procedural steps, into a so-called composite material that can be included into the manufacture of state-of-the-art refractories. The composite, represented as granulated material with its fine-scaled fractions and partly nano-scaled additive systems, is to be a key building block for the manufacture of refractories for iron foundries, since the material has to withstand temperatures of up to 1550 °C and is exposed to a variety of corrosive conditions. In general terms, one can say that in view of earlier installations, which can in principle be carried over to the recent time, refractory wear in a smelting aggregate is generally controlled by a combination of thermal, chemical and mechanical stresses. For instance, the infiltration and decomposition of refractory components constitute an essential mechanism of chemical corrosion, followed by transport via melting phases. In addition slag volume and characteristics significantly influences the wear. Typically exposed to temperatures round 1540 °C, the refractories have to withstand aggressive slags, varying furnace atmospheres (both reducing and oxidizing) as well as the liquid metal itself. At the same time, reactions and phase formations that may lead to wear and tear as well as destruction of the refractory lining must be reduced to a technically and, hence, economically acceptable minimum level. By today's standards these tough demands can be met by materials that are represented by the system SiO2-CaO-Al2O3. The resulting refractories are used in applications within the charge make-up zone and the shaft with their distinct resistance to hot abrasion and carbon monoxide. By adding carbon derived raw materials such as graphite, specifically processed coke or synthetic, in situ coking binders, exemplary shown in [4], refractory ceramics obtain the necessary resistance to process related corrosive, fused, but also gaseous media due to the characteristic wetting behaviour of carbon.

THE ALUMOSILICATE RAW MATERIAL

The "Eisenberger Klebsand" could be defined as a kaolinized quartz sand formally (technical term "luting sand") and represents a sedimentary kaolinite, which originated through rock decay (primary residual clay), de-solidification and rearrangements of the stratifications of variegated sandstone in the tertiary approximately 30 million years ago, also refer to [2], in which additional technological characteristics is presented. The "Eisenberger Klebsand" is mineralogically characterized through approximately 80 % quartz and 20 % clay minerals, combined with nano-scaled crystalline and non-crystalline phases, Tab. 1. The quartz grains covered with different kinds of kaolinitic minerals and also Al-Si-phases in an amorphous stage with fractions of µm- and sub-µm scales, Fig. 1. Already in a pure, untreated condition, the "Eisenberger Klebsand" as well defined AlumoSilicates (AS) combines high adhesion with increased mechanical strength in a wide range between room temperature and approximately 1700 °C. As predestined and versatile raw and refractory material, the "Eisenberger Klebsand" supports a wide spectrum of applications that encompasses both the entire foundry industry and metallurgical plants (also pig iron, especially coke ovens) beside the refractories industry. Interrelated deposits of luting sands are very rarely to find caused by the nature of earth.

All the more significantly, the luting-sand deposit located in the geological region called "Eisenberger Becken", represents the biggest world-wide and certifies the user a certain independence, through its geological uniqueness, from the international raw material market for long-time periods. A high-quality raw material refining and processing exist on approximately one square kilometre of an own territory with remarkable mineralogical and chemical constancy, that will anticipate an essential contribution also in future to the economical success of the industrial users.

Tab. 1: Characterisation of AlumoSilicates (AS)

	AS $_{coarse}$	AS $_{fine}$
Grain size distribution	d_{10} = 10 µm d_{50} = 230 µm d_{90} = 650 µm	d_{10} = 0,7 µm d_{50} = 4 µm d_{90} = 25 µm
Mineralogical composition	80% quartz 20% clay minerals	50% quartz 50% clay minerals + non-crystalline phases
Chemical composition	in wt.%	
SiO_2	91,3	70,5
Al_2O_3	5,9	19,6
Fe_2O_3	0,2	1,1
TiO_2	0,2	0,9
K_2O	0,2	0,9
Na_2O	0,0	0,1
CaO	0,0	0,1
MgO	0,1	0,2

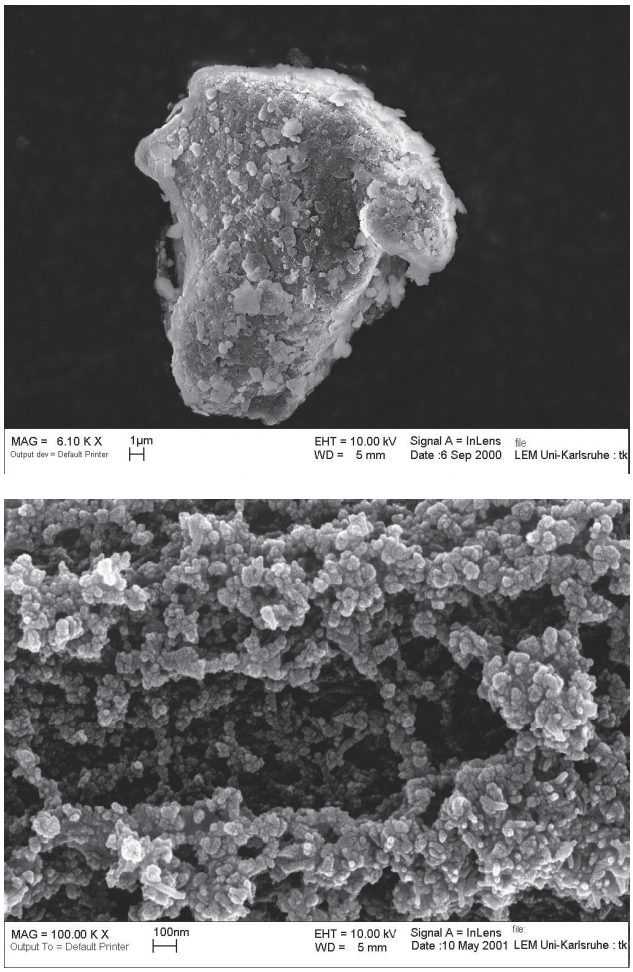

Fig. 1: Typical, irregularly restricted grain represented the alumosilicate from "Eisenberger Klebsand", surrounded by clay particles (upper illustration), structural construction of spherical Al-Si-gel-phases of a loosely connected aggregate (low illustration), from [3]

INNOVATIVE REFRACTORY SOLUTIONS

Key factor corrosion

Innovative refractory solutions made in Rhineland-Palatinate EKW GmbH, based in Eisenberg in the German federal state of Rhineland-Palatinate, works on the subject of innovative refractory solutions, from project management through installation to operations monitoring. The company focuses on technically efficient and economic solutions, providing its customers solutions ranging from cooperative material developments to modern application concepts. Moreover, combined system solutions are offered for the functional lining of shaft-furnaces with specific unshaped refractory materials and prefabricated products. EKA-CAST CSC and EKA-RAMMIX RSC are two recently established product ranges of unshaped refractory materials. Apart from synthetic and natural raw materials and carbon as common denominators, EKA-CAST suggests a refractory castable, while EKA-RAMMIX represents a ramming mixture or semi-plastic mix per definition. The primary target of development was set at developing a so-called corrosion-stabilised material system to face progressive chemical wear, especially in melting zones and siphons, in order to increase the life cycle of the melting shop, a feature that is already successfully established in the market. Type of furnace, operating conditions and installation requirements led to various specified products to be consistent.

HARMONIZING ECOLOGY, ECONOMY, AND LOGISTICS

As part of current studies, the rising demands on sustainable and environmentally compatible production of refractories were transferred into an objective to integrate the specific alumosilicate-ceramic raw material fractions in combination with selected carbonaceous ingredients based on recent procedural steps into composites which can be included into the manufacture of state-of-the-art refractory material [5]. This granulated material, Fig. 2, with its fine-scaled fractions and partly nano-scaled additive systems, is to be a key building block for the manufacture of refractories for iron foundries, since the material has to withstand temperatures of up to 1550 °C and is exposed to a variety of corrosive conditions. The reduced corrosion rate of the advanced, natural alumosilicate containing refractory materials is mainly due to the formation of a highly viscous melt at the interface between the corrosion medium, i.e. slag, and the ceramic surface as well as the low partial pressure of oxygen, which slows down the removal of solutes. Moreover the formation of the melting phase seals the refractory, leading to reduced carbon oxidation. Deep within the refractory ceramic, different PSD derived from alumosilicate of the

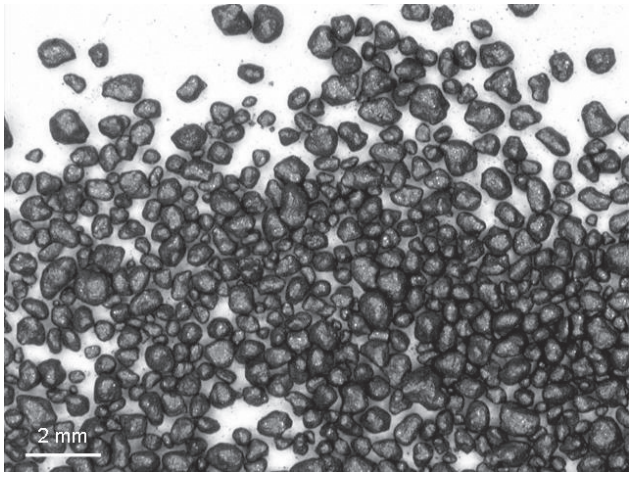

Fig. 2: Novel AlumoSilicate (AS) Carbon composite as an innovative and economic refractory solution

luting sand ("Eisenberger Klebsand") increase the resistance to oxidation by forming barrier layers in the carbonaceous matrix. As the temperatures of the pig iron are relatively low ranging between 1510 °C and 1550 °C, resistance to erosion and chemical corrosion, i.e. slag attack, is of more importance than high refractoriness, cf. synthetic raw materials. The "Eisenberger Klebsand" with its outstanding mineralogical characteristics and its differentiability has an elementary technical and economic potential for the development of innovative refractory products especially to support both the international one and the national but also the regional industry under consideration of the requirements of sustainable raw material supply.

OUTLOOK

From an economic and ecological perspective it can be written as a statement that applying the composite on the basis of alumosilicate of the luting sand ("Eisenberger Klebsand") provides the possibility of combining ceramic development technologies with a unique native raw material that is available on a long-term basis, with supplies of about 200 million tons of the alumosilicate raw material at the Eisenberg Palatinate deposit, Fig. 3. There has been evidence showing that the technical application of luting sand exemplary used in a composite with carbon has extensive industrial potential in the field of metallurgical melting technologies.

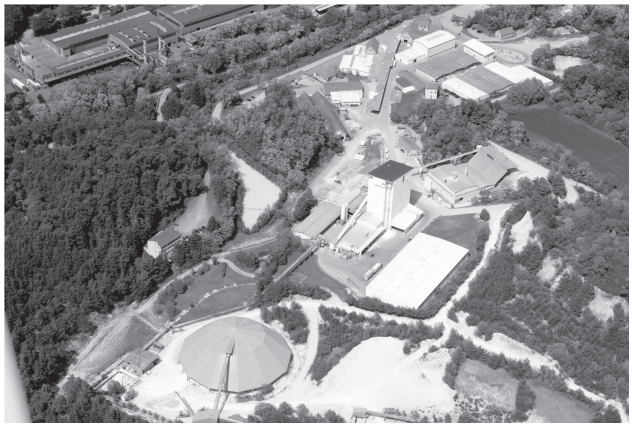

Fig. 3: The Rhineland-Palatinate Company EKW GmbH, Germany, with its own raw material deposit luting sand ("Eisenberger Klebsand") and high-end production facilities

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