

Mineralogical properties of metallurgical coke

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1 Introduction

Metallurgical coke is a key material for blast furnace (BF) ironmaking, acting as a major energy source (fuel), a reductant, a carburisation agent and a structural support [Andriopoulos et al. 2003]. Natural reserves of coking coal are limited and the standards for BF ironmaking are becoming increasingly strict, encouraging steel producers to implement environmentally friendly processes, while trying to maintain cost efficiency. In this regard, the production of high quality coke requires a better control of its properties e.g., reactivity and strength. The first parameter has a direct influence on energy efficiency of a BF operation (increase in reaction rate and decrease in reaction beginning temperature [Nomura et al. 2007]). Coke degrades during its descent through the BF. Degradation is caused by mechanical load, attrition, thermal stress, gasification reactions, inorganic compounds present in BF gases, and graphitization. Mineral matter in coke plays a major role in the character and extent of these degradation pathways, both directly and indirectly [Grigore et al. 2007].

2 Objectives of the research

This study is carried out within a framework of the research projects supported by the Academy of Finland and CORDIS (EU, RFSR-CT-2007-00001) and has the following major objectives:

- To identify the major mineral phases, their occurrence, crystalline features and composition in feed and BF coke (after loaded into the BF);
- To trace physical and chemical changes of coal-associated mineral phases during coking and BF processes;
- To reveal the nature of mineral phases \leftrightarrow gas reactions in BF coke;
- To evaluate the effect of volume changes and shape adjustments of mineral matter during phase decomposition, re-crystallization and polymorph transitions;
- To determine the properties of mineral matter on a surface of BF coke;
- To develop a mineralogical approach for enhancing properties of coke.

3 Results

3.1 Mineral phases in feed and BF coke

The major minerals in coals are quartz, carbonates (calcite, dolomite), feldspars, sulphides (pyrite) and a number of phyllosilicates, represented by clay minerals (kaolinite, montmorillonite, illite and halloysite) and micas. Analysis of literature data and our own studies [Gornostayev et al. 2008 and references therein] have shown that during coking process the minerals undergo: desulphurization ($\text{FeS}_2 \rightarrow \text{Fe}_{1-x}\text{S} \rightarrow \text{FeS} \rightarrow \text{Fe}$) - Figure 1a; decarbonation ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$), dehydration ($\text{Al}_4(\text{OH})_8[\text{Si}_4\text{O}_{10}]^* 4\text{H}_2\text{O} \rightarrow \text{Al}_4(\text{OH})_8[\text{Si}_4\text{O}_{10}] + 4\text{H}_2\text{O}$), dehydroxyla-

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tion ($K(Al)_2(OH)_2[AlSi_3O_{10}] \rightarrow K(Al)_2(AlSi_3O_{11}) + H_2O$), polymorph transformations (alpha-quartz \rightarrow beta-quartz \rightarrow beta-tridymite) and partial melting. The most common changes in mineral phases that take place in a BF coke are: polymorph transformations (beta-tridymite \rightarrow beta-cristobalite), melting and formation of glassy and new crystalline phases like spinel, mullite (Figure 1b; Table 1, analysis 1) and corundum. The other synthetic equivalents of minerals that have so far been found in tuyere coke but are not observed in primary coke are: gupeite - Fe_2Si ; xifengite - Fe_5Si_3 ; schreibersite - Fe_3P ; barringerite - Fe_2P ; oldhamite - $(Ca,Mg,Fe,Mn)S$ and fersilicite - $FeSi$ [Gornostayev and Härkki 2005].

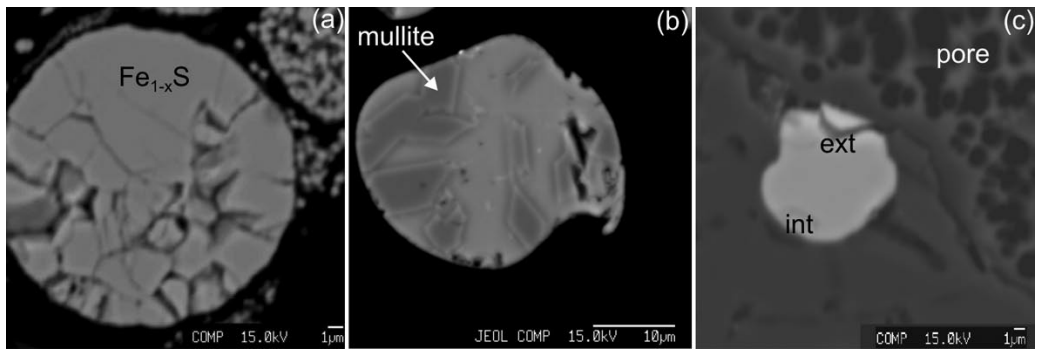


Figure 1 a) $Fe_{1-x}S$ in a coke matrix (sample c-17, scale bar 1 μm); b) crystal of mullite in glassy phase (sample 0840_175-200, scale bar 10 μm ; Table 1, analysis 1); c) SiO_2 grain exposed to internal pore (sample 30424109-150, scale bar 1 μm ; int. - internal zone, ext. - external zone - see Table 1, analyses 2 and 3).

3.2 Mineral - gas reactions in a BF coke

Scanning electron microscopy and electron-microprobe analysis of samples of the BF coke have revealed [Gornostayev et al. 2007] Al-saturation and alkalinization of SiO_2 (especially grains smaller 10 μm) by BF gas phase circulated in pores of the coke (Figure 1c; Table 1, analyses 2 and 3). Thermodynamic calculations for 100gsolid/100ggas and temperatures 800–1800°C have shown that the major BF gases (CO , N_2 , H_2) have no effect on the alkalinization of SiO_2 . We suggested that “the addition of fine-grained quartz to the surface of the coke before charging a BF can remove some of the Al and alkali from BF gases and reduce coke degradation by alkalis, or at least improve its properties until the temperature reaches approximately 2000°C. Some addition of kaolinite to feed cokes with a high K+Na content and low Al/(K+Na) can probably facilitate the longer retention of alkalis in a Si-Al-K-Na-O melt” [Gornostayev et al. 2007].

3.3 Volume and shape changes of mineral matter

The structural changes of feed and BF coke, in particular [Kerkkonen 1997], include the expansion of meta-clays and swelling and balling-up of aluminosilicates. These processes are accompanied by dehydration and dehydroxylation of phyllosilicates and the subsequent crystallization of mullite can cause considerable density changes. The density values (g/cm^3) of montmorillonite (2.35), halloysite (2.57), kaolinite (2.60) and illite (2.75) are lower than that

of mullite (3.05), which will be formed from these minerals. It should also be noted that illite is 17% denser than montmorillonite. From this point of view, the clay mineral with the lower density can eventually cause the appearance of more cavities in the coke, thus reducing its strength [Gornostayev et al. 2009]. Data on dehydration and dehydroxylation temperatures, including those for different heating rates, can be used to assess the optimal pre-heating temperature for a coal mix. The melting of mineral phases leads to the formation of alkali- and Ca-bearing aluminosilicate spherules and irregular slag segregations (Figure 2a; Table 1, analyses 4 and 5). The formation of these particles does not destroy the coke matrix, since they adjust their shape inside the pores (Figure 2a) and move towards the surface (Figure 2b) of the coke [Gornostayev and Härkki 2006a]. It was also observed that the octahedral spinel crystals can cause the formation of cracks in BF coke that will reduce its strength [Gornostayev and Härkki 2006b]. From this point of view, a high Mg content in the coking coal was considered as negative for the CSR value of the coke.

Table 1 WDS analysis of mineral particles in the BF coke*

	Na ₂ O	K ₂ O	MgO	CaO	Al ₂ O ₃	FeO	ZnO	SiO ₂
1	0.92	2.40	0.61	0.17	54.45	0.01	0.00	42.53
2	0.77	2.54	0.24	0.05	15.68	0.01	0.02	78.93
3	1.46	2.68	0.28	0.06	16.10	0.03	0.02	78.00
4	0.41	0.40	0.07	18.18	24.93	0.00	0.05	55.08
5	0.16	0.12	0.06	22.72	22.82	0.05	0.03	53.99

* 1 – crystal of mullite (Fig. 1b; sample 0840_175-200); 2, 3 – altered SiO₂ (2 - internal zone, 4 analyses; 3 - external zone, 3 analyses; Fig. 1c, sample 30424109-150); 4 – spherule (Fig. 2a, sample 0840_75-100); 5 – segregation of slag (Fig. 2a, sample 0840_75-100). Jeol JXA-8200, University of Oulu.

3.4 Mineral matter on a surface of BF coke

Mineral phases of the BF coke cause the appearance of inorganic coating on its surface (Figure 2b), and the re-distribution of mineral matter inside the coke leads to the formation of a “two-phase” system comprising (1) mineral matter and (2) a mineral-free carbon matrix.

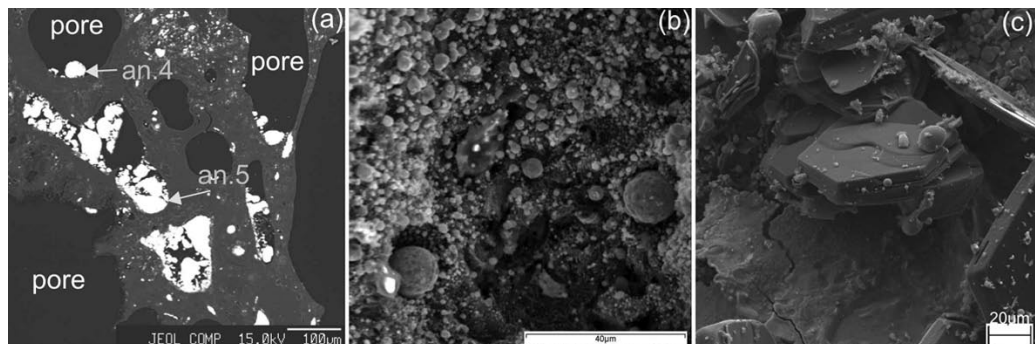


Figure 2 a) aluminosilicate spherules and slag segregations in the BF coke (sample 0840_75-100, scale bar 100 μm; see Table 1, analyses 4 and 5); b) aluminosilicate spherules on a surface of the BF coke (sample 30424109-15, scale bar 40 μm); c) graphite crystals on a surface of the BF coke (sample 0840_25-50, scale bar 20 μm).

The ability of the inorganic compounds for re-distribution and the formation of a mineral coating depends on the melting temperature of a particular mineral phase and on the viscosity of the molten material [Gornostayev et al. 2006a]. A less viscous melt can migrate for longer distances within the coke to provide more material for covering its pores and surface. Particles of mineral phases with a lower melting temperature will appear on the surface of a piece of coke in the early stages of coke consumption, and will cause the earlier formation of weak spots and reduce the reactivity of the coke by limiting the surface available for reduction reactions. The formation of graphite crystals (Figure 2c) is also common for the BF coke [Gornostayev and Härkki 2007]. The process possibly decreases reactivity of the BF coke and it can be accompanied by the generation of fines. The graphitic coating on a surface of BF coke can act as a lubricant affecting the mechanical stability of the coke cone in BF.

4 Relevance of the research

The results of the research can be used for:

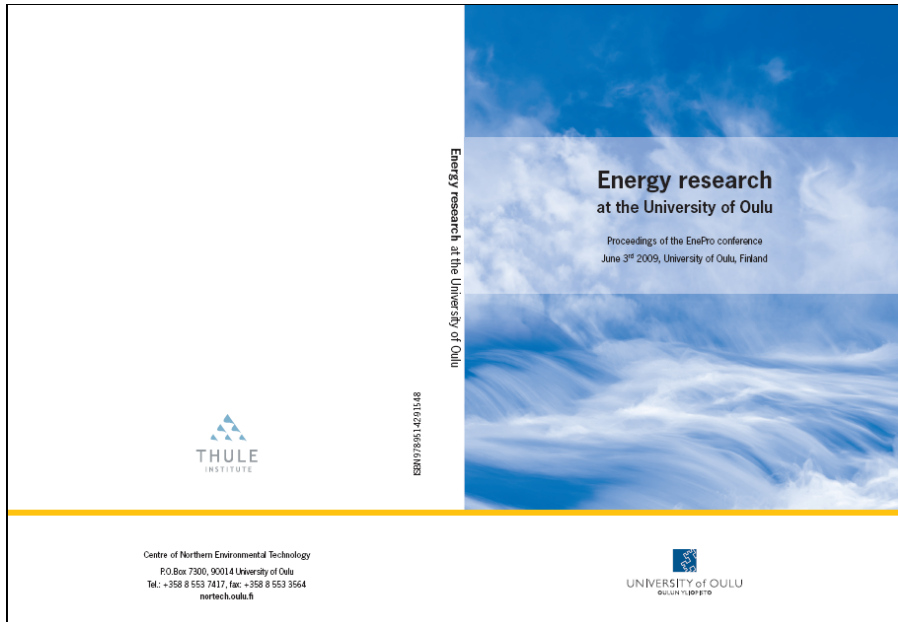
- Recognition of effect of a particular mineral in coal on properties of coke and its behaviour in a BF;
- Preparation of guidance for selection of coal blends for coking purposes and adjusting the coking conditions (temperature, preheating rate, etc.);
- Collection of data (digital photographs, SEM and BSE images, X-Ray maps, WDS and EDS analyses), which can be used for future projects and educational purposes.

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