PROCESS ORIENTED CHARACTERIZATION OF OOLITIC IRON CONCENTRATE DURING DEPHOSPHORISATION BY ROASTING AND LEACHING

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ABSTRACT

Phosphorus in iron ores is considered as a deleterious component to iron making reflecting in cold shortness of the produced steel. The present study investigates the phosphorus migration pattern resulting from thermal treatment of an oolitic-type iron concentrate with and without additives. To this end focused mineralogical and microscopic observations were performed. The results have shown that roasting with alkaline additive drives phosphorus outside the hematite hosting mineral, however it remains evenly distributed inside the volume of the oolites. It penetrates inside the newly formed cementing phases of Al-Na-Si-Fe-type and also fills the interstices between the crystals. Other than phosphorus, aluminum, calcium and iron tend also to migrate towards the amorphous-type cementing phase. Finally, the possibilities for P removal by means of magnetic separation and acid leaching of the roasted concentrate were evaluated. The obtained final product presents a standard iron concentrate suitable for steelmaking with its phosphorous being dropped from 0.71% to 0.05% and iron grade of a nearly 66% being reached.

KEYWORDS

Iron ore, phosphorous removal, roasting, characterization
INTRODUCTION

Significant proven reserves of iron ores are still not exploitable due to lack of an economically viable and efficient technology for removal of phosphorus. Among them are the oolitic iron ores with high phosphorus which are estimated to nearly 377 billion tons (Hernandez et al., 2012). Phosphorus is a deleterious component giving a cold shortness to steel and often is penalized if exceeding 0.07%. Most of the high-P iron ores are considered refractory since phosphorus is finely disseminated and is evenly met as phosphate groups inclusions inside the limonite structure. Studies on inclusion of phosphorus in artificially synthesized goethite have shown that it is adsorbed as \([\text{HPO}_4]^{2-}\) groups bridging the adjacent iron ions (Parfit et al., 1975). The high-phos iron ore originating from Lisakovsk deposit, Kazakhstan presents a similar mineralogical issue because the quantity of P, met as solid solution, is substantially higher than the one in P-containing minerals. A potential reason for that is the ore body formation process from the slow deposition of iron-rich precipitates together with clastic erosional sediments in rivers. There is significant quartz and clays inside and around the oolites. The deposit contains about 1.7 billion tons of measured and indicated reserves at 35–41% iron and 1.1 billion tons of inferred ore have been delineated possessing nearly the same chemical composition (Golubovskaya, 2003; Kokal et al., 2003).

A study upon the phosphorus associations in an ore coming from Hamersley Province, Australia has shown that the majority of P is occurring in occluded form as \([\text{PO}_4]^{3+}\) species or discrete P-bearing minerals, sub-micron in size, accumulated in ultra-fine micro-pores or in intra-domain regions between goethite crystallites. Goethite can accommodate into its structure some trace elements as well, where the process of replacement has been controlled mainly by the ionic radius and to a lesser extent by the cation valence (Wells & Ramanaidou, 2011).

Plenty of studies have indicated that without thermal treatment the removal of phosphorus is quite inefficient, accompanied by significant iron losses (Kokal et al., 2003, Fisher-White et al., 2009, Edwards et al., 2011). The two main directions for phosphorus removal from iron ores used in steelmaking could be summarized as: 1) addition of alkali or alkaline earth compounds before Direct Reduction of Iron (DRI), besides volatilization the process includes magnetic separation; and 2) thermal process at lower temperatures using additives followed by physical separation and acid leaching.

The first route aims to remove phosphorus, for example by reduction with syngas in a rotary heart furnace. An experimental work on gas-based DRI process shows that phosphorus could be reduced from 1.25 to 0.27% with carbon monoxide as reductant and to 0.33% with hydrogen (Tang et al., 2010). There is a great diversity of research works devoted to removal of P after metallization by solid reductant. A satisfactory rate of metallization at temperatures 1100–1250°C has been achieved but only 10% of the phosphorus has been removed. The optimal temperature in these tests attaining 85% removal of P is found to be 1280–1300°C, with addition of 10% CaO which reflected in P decrease from 1.66 to 0.24% (Han et al., 2012). Similar tests are carried out in SL/RN kiln at temperature higher than 850°C with lignite coal and CaCl$_2$ additive (Hernandez et al., 2012). As a result, a decrease in phosphorus from 0.6 to 0.12 has been achieved. A deeper removal of phosphorus is achieved by two-staged magnetic separation after metallization with mixture of Na$_2$SO$_4$ and Na$_2$CO$_3$. The metallized iron ore is ground to 67% - 0.074 mm before the first stage and reground further to 97.15% –0.025 mm. About 20% of P is removed by volatilization and the rest is removed by magnetic separation lowering phosphorus from 0.83 to 0.06% (Xu et al., 2012). The addition of borax to the sodium salt is leading even to higher rates of dephosphorization. Comparison of leaching efficiency of high-P iron ore metallized as green pellets at 1050°C with and without additives shows that from iron ore with 48.96% Fe and 1.61% P a magnetic concentrate with 85.1% Fe and 0.97% P could be obtained without additives. When additives are used, iron recovery of 92.5% with 92.7% Fe and 0.09% P was achieved (Li et al., 2013). A flowsheet comprising roasting followed by grinding and low intensity magnetic separation has been tested for dephosphorization of limonite iron ore from Huimin, China, having 34% Fe and 0.80% P (Bai et al., 2012). The method has involved blending of the ore with 20% carbon and 10% Na$_2$O, followed by thermal treatment at 1050°C for 150 min and clinker grinding to 90%, –38 μm. The iron concentrate obtained contains 76.5% Fe and 0.25%
P at 76.3% recovery. In general, after metallization with the above mentioned additives a good rate of
dephosphorization can be achieved by magnetic separation after very fine grinding of the clinker.

The second dephosphorization route aims at P removal ahead of metallurgical process. The
advantage is based on the lower solubility of P in magnetite and the already proven high efficiency of its
leaching from an iron ore roasted with additives (Feld et al., 1966). The influence of low temperature
roasting on the acid leaching of phosphorus is investigated with the best result of 97.3% removal achieved
after leaching for one hour with 1M H₂SO₄ at boiling temperature, but on expense of 71.1% weight loss. A
better recovery of iron is obtained when the percent of solids in leaching was increased from 0.5 to 25%
(Edwards et al., 2011). The temperature of roasting is also an important factor and comparative tests
between samples roasted at 300–350°C and 900°C have shown undoubtedly that higher temperatures gave
better results (Fisher-White et al., 2012). A great variety of studies have been also carried out on
dephosphorization of the Lisakovsksky gravity-magnetic concentrate. After roasting with and without
additives various leaching options (aqueous, alkaline, acid, ambient or in autoclave, etc.) were tested
(Belikov et al., 2003; Kokal et al., 2003). Based on these studies leaching plant with 900,000 t annual
capacity has been built, however operations have been seized since the targeted level of P in the final
product (0.17–0.20%) has not been achieved.

The aim of the present study is to investigate, by using variety of characterization tools, the
phosphorus migration patterns in the oolite-type iron concentrate following its treatment in alkaline media.
It is anticipated that both the phosphate groups from the limonite and the gangue minerals (mainly oxides)
will react with the roasting agent forming new phases which will capture substantial part of phosphorous
enabling its downstream removal.

EXPERIMENTAL

Materials and Methods

The high phosphorus oolitic iron concentrate originates from the Lisakovksky mine in Kazakhstan.
The ROM processing flowsheet at the mine site encompasses jiggling and wet high intensity magnetic
separation. The main gangue mineral is quartz observed inside and outside the oolites. The oolite matrix is
seen as clayey substance with particles below 5 µm in size consisting of quartz, smectite, mica, kaolinite,
chlorite, birnessite and goethite (Golubovskaya, 2003). The percentage of a distinct phosphorus bearing
minerals varies for the different parts of the deposit, but is always substantially lower than its total
concentration. The chemical composition of the investigated concentrate is as follows: 49.16% Fe, 9.97%
SiO₂, 4.68% Al₂O₃, 0.71% P. The average particle size is 0.394 mm.

A representative sample of the concentrate taken by a rifle sampler was divided into 11
subsamples. To investigate the transformation pattern of the minerals, input material was heated from 100
to 1000°C with a step of 100°C inside a muffle furnace at open air. For the roasting procedure, samples are
poured in ceramic crucibles and placed inside a muffle furnace, then heated to 900°C for one hour with and
without NaOH addition. The ore/additive mixture was prepared in advance by adding 38% NaOH solution
to the sample, calculated as 10% on a dry basis, mixing and letting to dry at 105°C. To outline the effect
from roasting on phosphorus removal two representative samples of 1.6 kg were likewise roasted for one
hour at 900°C with and without NaOH, after which were left to cool down to room temperature for 16
hours. Then preliminary phosphorous removal tests (leaching / magnetic separation) were carried.

Leaching was done in 500 mL beaker at 400 rpm stirring, while magnetic separation using a
laboratory unit with permanent Nd₂Fe₁₄B magnets generating induction of 0.34 T inside the separation
zone.

Characterization

Representative samples (approximately 5 g) were cold mounted in epoxy resin, ground and
polished by an automatic grinding/polishing machine. Then the polished-sections were covered by
evaporated carbon to render them conductive and suitable for SEM analysis. The migration of phosphorus in and around the oolites is investigated by a FEI Quanta 400 SEM with a coupled energy dispersive X-ray spectrometer (EDX) Bruker Nano Quantax 800 system. Micrographs were acquired through back-scattered electrons (BSE) detector, which produces images of polished specimens with atomic number contrast (Goldstein et al., 2003).

For the quantitative XRD analysis nearly the same quantity of sample was ground using a McCrone micronizing mill with agate grinding media for 10 minutes in ethanol following a standard procedure preventing the crystal structures from damages while effectively reducing particle size to below 10 µm (Dermatas et al., 2007; Kleeberg et al., 2008). The samples were discharged into PTFE Petri dishes and dried at 343°K in a vacuum oven. When dry, samples were gently reground with pestle in an agate mortar and hackloaded into sample holders for X-ray diffraction analysis, performed on a Bruker-AXS D4 Endeavour diffractometer with Co kα radiation, Fe kβ filter and a LynxEye position sensitive detector (PSD). Spectra were acquired from 4 to 105° 2θ at 0.02° steps, for 1 s per step, resulting in accumulated 183 s per step due to the PSD. The identification of all the minerals was done with Bruker-AXS’s DIFFRAC.EVA suite and PDF4+ 2012 relational database (ICDD, 2012). Mineral quantification based on Rietveld method with a fundamental parameters approach (Cheary and Coelho, 1992) was performed on a Bruker-AXS’s Topas 4.2 software. Crystal structure information for the minerals was supplied by the Bruker Structure Database. Refining was performed considering seven emission lines for kα and one for kβ, as the Fe filter does not remove all kβ radiation. Background was calculated by a fifth order polynomial and Lorentz polarization was fixed at zero. For most of the minerals, only the lattice parameters, the scale factors and the Lorentzian contribution to crystal size were allowed to be refined. Two generations of goethite were established and the crystal size parameter was adjusted to allow for refinement of both types without excessive correlation. Goethite was divided into coarse (50–10,000 nm) and fine (<30 nm). Isomorphous Al-for-Fe substitution was refined following Knorr and Neumann (2012). The coupled Al-for-Fe and OH-for-O2- substitutions in hematite were refined following the procedure of Neumann and Avelar et al. (2014). The oxidation state of the iron in the magnetite-maghemite solid solution was refined based on the method of Neumann and Medeiros (2015) derived from data of Gorski and Scherer (2010).

The chemical analysis of the non-treated concentrate and the products after beneficiation were realized by sequential XRF, XP spectrometer ARL 9400.

**RESULTS AND DISCUSSION**

**Structural Changes Caused by the Thermal Treatment**

The XRD analyses of the samples heated at temperatures from 100 to 900°C are combined and presented at Figure 1.

![Figure 1 – Effect of treatment temperature on mineral transformation](image-url)
The analysis of the thermally treated samples (Figure 1) shows that the conversion process is running towards complete disappearance of goethite and siderite peaks and their replacement by hematite ones. The quartz peaks are also sharper and well distinguished, especially at elevated temperatures. Peaks of associated minerals are hardly to be distinguished from the background; however they have been subsequently detected by a quantitative XRD analysis. Table 1 reports on the mineralogical composition of the input concentrate and the same one roasted with and without NaOH.

Table 1 – Phase transformations inside roasted without and with NaOH oolitic concentrate determined by a quantitative XRD analysis (wt%)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Feed</th>
<th>Without NaOH</th>
<th>With NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite fine</td>
<td>78.5</td>
<td>–</td>
<td>6.6</td>
</tr>
<tr>
<td>Goethite coarse</td>
<td>2.7</td>
<td>–</td>
<td>0.7</td>
</tr>
<tr>
<td>Hematite</td>
<td>5.6</td>
<td>87.2</td>
<td>77.4</td>
</tr>
<tr>
<td>Siderite</td>
<td>2.1</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Quartz</td>
<td>8.7</td>
<td>9.1</td>
<td>4.3</td>
</tr>
<tr>
<td>Titanite</td>
<td>0.9</td>
<td>0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Anatase</td>
<td>0.4</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Zircon</td>
<td>0.4</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Monazite</td>
<td>0.5</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Na-silicate</td>
<td>–</td>
<td>–</td>
<td>2.7</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

The results above suggest that sodium hydroxide reacts with quartz and zircon as well as with clay minerals. The sodium silicate is detected as $Na_2H_2SiO_4\cdot2H_2O$ implying that it reacts vigorously with the water released from the goethite and also with the moisture accumulated probably from the air during cooling. A special attention deserves the fact that 7.3% of the goethite remains unchanged after heating to 900°C in the presence of sodium silicate. It could be assumed that the latter one is melted and encapsulates the oolites thus obstructing the complete water liberation and preventing phase transformation. The transition of goethite to hematite during the thermal treatment involves formation of intermediate phases of protohematite (250–400°C) and hydrohematite (430–700°C) before an ultimate transformation to hematite to take place (> 800°C) (Wells et al., 2006). Traces of siderite remain in the roasted without additives product. The NaOH addition is below the stoichiometric requirement for the complete reaction with silica. Therefore part of di-aluminium three-oxide and quartz remains unchanged. Observations show that after the thermal treatment titanium is present mainly as anatase TiO$_2$, titanite CaTiSiO$_5$ and rutile TiO$_2$. After liquefaction of the sodium silicate titanate is degraded to rutile while the rest is included in amorphous cementing phases of Al-Na-Si-Fe-type. As a rule, zirconium should vary around its Clarke, while titanium appears in clays and oolites in twice higher concentration (Golubovskaya, 2003).

**Substitution of Fe$^{3+}$ with Al$^{3+}$ ions**

An interesting feature of the Lisakovsk ore is the fact that part of the iron in goethite structure is replaced by aluminium ions. This affinity is predetermined by the close ionic radius of Fe$^{3+} = 0.65$ Å and Al$^{3+} = 0.54$ Å. To quantify the isomorphic substitution of Fe$^{3+}$ ions with Al$^{3+}$, the amount of hercynite FeAl$_2$O$_4$ has been measured. The rate of substitution of Fe$^{3+}$ with Al$^{3+}$ ions was investigated for the three samples discussed above with the results being displayed in Table 2.
Table 2 – Al$^{3+}$-for-Fe$^{3+}$ substitution in goethite and hematite after roasting with and without NaOH (10% w/w)

<table>
<thead>
<tr>
<th>Substitution in:</th>
<th>Feed</th>
<th>Without NaOH</th>
<th>With NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$ in goethite</td>
<td>0.07993</td>
<td>0</td>
<td>0.36</td>
</tr>
<tr>
<td>Al$^{3+}$ in hematite</td>
<td>0.359</td>
<td>0.04809</td>
<td>0.009213</td>
</tr>
<tr>
<td>Fe$^{3+}$ in hematite</td>
<td>0.491</td>
<td>0.9519</td>
<td>0.9908</td>
</tr>
</tbody>
</table>

The high rate of substitution of Al$^{3+}$-for-Fe$^{3+}$ in goethite and the even higher in hematite is linked to the particular mineralogy of the Lisakovsk iron ore. However, this trend could not be valid through the entire zonation of the deposit. It could be seen that the remnants of goethite roasted with NaOH contain 4.5 times higher Al$^{3+}$ substitutions. For the hematite a reverse trend could be distinguished, suggesting that the thermal treatment and the addition of alkalis do stimulate repulsion of Al$^{3+}$ ions outside the crystal lattice. It was established that Al$^{3+}$ ions react with the sodium hydroxide through formation of sophisticated Na-Al-Si-O cementing phases which are hardly to be identified by XRD due to their amorphous character. The phosphorus migration towards these phases is commented in the section below.

Migration of Phosphorus inside the Oolites

SEM-BSE images of oolites before and after roasting are shown in Figures 2 and 3, respectively, with inclusions of monazite (Ce, La, Nd)PO$_4$. The spectrum shown in Figure 2 suggests that negligible part of the phosphorus is present as grains of thorium-free monazite. As a rule, light rare earth elements (Ce, La and Nd) are carried predominately by monazite, with similar observations being reported for Brockman iron formation in Australia (Morris, 1973). The chemical composition of the chosen spots shows Ca presence, possibly due to the apatite Ca$_5$(PO$_4$)$_3$OH being met within the closer neighbourhood.

Figure 2 – Monazite inclusion in oolite seen in unroasted concentrate: Left - BSE image, right - EDX spectrum at the point indicated with an arrow
The results shown in Figure 3 suggest that the thermal treatment provokes cracks generation and oolites fragmentation, however without influencing monazite grains. The spectra in Figure 3 (b) and (c), show titanium minerals also, detected in close vicinity to the monazite grains. Phosphorus has been detected as apatite and wavelite as well, but the concentration of these two minerals is low compared to the overall P content. Few hypotheses could be suggested based on the observed close relationship between iron and phosphorus content. Either the phosphate groups or P$^{5+}$ ions with radius 0.38 Å forming solid solution are captured by bridging or substitution inside the limonite structure (Parfit et al., 1975) or P-bearing minerals as nano-sized crystals enter as inclusions in the oolites (Wells, Ramanaidou, 2011). The physical separation of Lisakovsk ore is leading to phosphorus increase from 0.4–0.6% to 0.7–0.9% in the obtained concentrate (data not shown).

It could be argued, that sodium silicate when used as alkaline roasting agent at temperatures above its point of liquefaction does accumulate part of the phosphorus inside the newly formed amorphous material. After cooling of the roasted concentrate, this is leading to aggregation of the oolites at macro-level. Due to water liberation, iron minerals restructuring and chemical reactions taking place, the oolites experience intensive cracking which stimulates phosphorus migration inside the newly formed structures. These effects are evidenced in Figure 4, while Table 3 presents the chemical composition of the selected points on the oolite surface marked in Figure 4.
The first three points are located inside the core of the oolite where the levels of Na and Si are substantially lower. As to phosphorous it could be noted that its highest concentration is detected around the center of the oolite (point 1), where the structure is still intact. At points 2 and 3 close to the oolite periphery, phosphorous is found as 0 and 0.54%, respectively. At points 4 to 7, sodium prevails over silicon, indicating zonation of high alkalinity. The fact that phosphorous is detected at these points is suggesting that it has migrated from the core towards this zone, since the free quartz particles in the non-roasted concentrate obviously do not bear phosphorous. Other than phosphorus, Al, Ca and Fe tend also to migrate through this amorphous-type cementing phase. Therefore, provided the phase is separated by physical means, a substantial loss of iron could be expected. In the presence of Na, the melting point of quartz is dropped from 1670°C down to approximately 700°C, which stimulates the molten Si-bearing liquors to envelope the oolites and to penetrate inside the formed cracks.

Implications for Phosphorus Removal

Some important guidelines regarding the design of potential flowsheet could be drawn from the above findings: (1) the addition of sodium leads to creation of alkaline media which accumulates substantial part of phosphorus; (2) the roasting should be carried out with reductant offering high level of liberation at lower iron losses; (3) more profound phosphorus removal could be achieved only through combination of physical and chemical separation. Based on the above considerations, tests on dephosphorization were carried out at laboratory scale involving roasting with 10% NaOH and 8% coke at 900°C for one hour, grinding, water leaching and magnetic separation. The concentrate is dried and leached in 10% sulphuric acid at 40% solids for 15 minutes at room temperature and continuous stirring. The process is accompanied by magnetic separation with the resulting magnetic fraction presenting a dephosphorized iron concentrate with phosphorus being dropped from 0.71 to 0.05%. The concentrate contained nearly 66% iron with the rest being presented as follows: SiO₂ 4.15%, Al₂O₃ 2.16%, Na₂O
0.33%, MgO 0.2% and Mn 0.2%. Iron recovery of 92.43% is thus achieved with 90.44% of the phosphorus being removed. A sample from the concentrate was examined by SEM-BSE – Figure 5.

![Figure 5 – SEM-BSE view of iron concentrate (upper left) and EDS analysis inside points a, b and c](image)

Within the examined three points seen in Figure 5, only iron and oxygen have been detected. At point “a”, however, a peak of aluminum appears with an overall content of 2.16%. The result testifies that the chosen operational sequence is the right one which warrants further up-scaling studies.

**CONCLUSIONS**

Focused characterization on oolitic type high-phos gravity magnetic iron concentrate subjected to alkaline roasting has been performed. It has been found that the phosphorous met in the limonite oolitic structures could be driven out towards newly formed amorphous phases provided they have a strong alkaline reaction. Other than phosphorus, Al, Ca and Fe tend also to migrate into this amorphous-type cementing phase. Therefore following an alkaline roasting, the subsequent phosphorous removal could be realized through magnetic separation and acid leaching. The obtained final product with 0.05% P and 66% Fe meets the requirements not only for blast furnace process, but also for direct reduction of iron use.

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