

# REMOVAL OF PHOSPHORUS THROUGH ROASTING OF OOLITIC IRON ORE WITH ALKALINE EARTH ADDITIVES

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## ABSTRACT

The present study is devoted to improvement of the leaching efficiency during phosphorous removal from high phosphorous gravity-magnetic concentrate. Before leaching the concentrate has been subjected to roasting with the addition of either  $\text{Ca}(\text{OH})_2$  or  $\text{CaO}$ . The oolitic iron ore is roasted at  $900^\circ\text{C}$  for one hour. This reflects in reaction between alkaline earth additive and quartz, aluminosilicates, phosphorus, and some other minor components of the gangue minerals. The application of leaching, physical separation, and wash out of salts has resulted in the decrease of phosphorus from 0.7 to 0.15 % and it is established that the major influencing factor is the concentration of acid and to a less extent duration of the leaching process. About two third of the phosphorus can be removed by roasting with 3 %  $\text{CaO}$  to hematite, coarse grinding to  $d_{50}$  0.3 mm, dry high intensity magnetic separation and leaching of the magnetic fraction with hydro-chloric or nitric acid.

**Keywords:** roasting, leaching, magnetic separation, oolite, goethite

## INTRODUCTION

The iron ore deposit at Lisakovsk, North Kazakhstan, is a limonitic one of oolitic type and the major iron minerals are goethite and about 0.5 % magnetite. The gangue minerals are predominantly quartz and clay like minerals such as carbonates, chlorite and other aluminosilicates as reported in a comparative study by Kosava *et al* (1966). The phosphorus content in the iron concentrate is about 0.6 – 0.8 % and the studies has shown that it is not represented as separable from iron minerals species, Belikov *et al* (2002), Ionkov *et al* (2011) but is included in limonite as a solid solution. Attempts for physical separation of phosphorus from similar Australian iron ore performed and commented by Gooden *et al*, (1974) have failed since phosphorus was included as phosphatic groups  $[\text{PO}_4]^{3-}$  in the structure of the limonite. At the Lisakovsk GOK, an experimental hydrometallurgical plant for dephosphorisation of the iron gravity-magnetic (GM) concentrate with an annual capacity of 580 000 tones is erected as reported by Kokal and Farais (2008). Following several trials and technology adjustments the plant has been placed in operation during late 2011. The implemented technology includes roasting at  $900^\circ\text{C}$  in neutral media to hematite followed by dry high intensity magnetic separation and leaching in pachucas with sulfuric acid. The above dephosphorisation technology is developed by Belikov *et al* (2003) at the “Mekhanobr Engineering” AO and laboratory tests have shown that the level of phosphorus can be decreased down to 0.15 – 0.20 %. Unfortunately, up to now, such level of P removal is still not attained at plant scale.

Studies on the direct leaching of phosphorus using mineral acids have shown that the process is slow and is taking place only on particle surfaces leaving quite significant unreacted core. At the beginning of the thermal process, water captured in limonite is released and at temperatures  $370 - 390^\circ\text{C}$  goethite is transformed into

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hematite. In reductive media and at temperatures higher than 800°C magnetite or maghemite are formed. The solubility of phosphorus in these minerals is substantially lower and they are concentrated along the newly formed cracks and surfaces as blebs, as reported by Gooden *et al* (1973, 1974).

Muhammed and Zang (1989) have used nitric acid (6M) leaching for 24 hours of a magnetite iron ore containing 1 – 3 % P presented as apatite and have claimed a drop in phosphorus level below 0.05 %. The same authors have stressed that the main problem during leaching has been gypsum precipitation and the contamination of iron concentrate with sulfur. An efficient removal of phosphorus down to 0.05 % from high P iron ores is reported by Forsberg and Adolfson (1981). In this study P was also present mainly as apatite and its leaching was carried out with 2M HCl and 2 – 6 M HNO<sub>3</sub> at temperatures between 10 and 60°C and duration of up to 30 hours. Leaching after roasting to 300°C has been tested with Australian iron ores rich in phosphorus present as apatite by Edwards *et al* (2011). Results have reported that up to 44 % of P can be removed without pre-heating when 1M sulfuric acid solution was used as leaching agent. At boiling point temperature, a removal of up to 97.3 % can be achieved but on the expense of high degree of iron dissolution. Unfortunately, the best results reported at lab scale are still far from economic viability. The approach of Zhu *et al* (2010) for dephosphorisation of high P oolitic iron ore from Chinese deposit includes briquetting with coal, roasting at 800°C, magnetic separation and leaching with sulfuric acid. The main phosphatic mineral is often incorrectly referred as “collephanite” Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub>·H<sub>2</sub>O which was transformed into carbonate apatite during roasting. Removal of phosphorus was carried out in two stages. The first one was magnetic separation after grinding to 93.6 % - 0.075 mm which facilitated 72.58 % of P to be removed and the second stage has encompassed leaching for two hours where P level has been decreased from 0.43 to 0.23 %. Akatov *et al*, (1969) have approached the dephosphorisation problem of Lisakovsk concentrate by heating it to 850 – 950°C in the presence of NaOH and then subjecting it to water leach, thus bringing a final concentrate with 0.14 - 0.17 % P. The behavior and the transformation of phosphorus at increased CaO/SiO<sub>2</sub> ratios in the iron ore during sintering was investigated by Khasen (2005), who reported that P could participate in formation of new mineral phases, namely silicocarnotite Ca<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>(SiO<sub>4</sub>) and nagelschmidite Ca<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. At temperatures higher than 1100°C developed during sintering, phosphorus is dissolved inside the molten fayalite where its concentration increases to 4.3 – 7.4 %. Conclusions have been made that the olivins are highly resistant to acid leaching and phosphorus removal during these tests has never exceeded 12 %. Feld *et al*, (1966) have tested roasting in the presence of metal halides such as calcium, zirconia, manganese, copper, lithium etc. at temperatures between 500°C and 1200°C. The optimum temperature reported in the study has been 900°C. Studies upon the influence of alkali and earth alkaline additives were reported as well by Fisher-White *et al* (2009), Ionkov *et al* (2011), etc.

The presented results originate from research aiming at improved phosphorus removal from the Lisakovsk gravity-magnetic concentrate. The idea behind our approach is to transfer and transform the phosphorus met in limonite as solid solution into apatite or other mineral(s) which apart from calcium, might contain silicon, iron, aluminum etc., and then to subject these mineral formations to acid leaching.

## EXPERIMENTAL

### Origin of the gravity magnetic concentrate and its characterization

The sample under study originates from the beneficiation circuit of the Lisakovsk (Kazakhstan) iron ore processing plant and is used as received. It is further denoted in this study as GM (gravity-magnetic) concentrate. Chemical analysis of the concentrate before and after leaching has been done using a sequential XRF XP X-ray spectrometer ARL 9400. For tracking the mineralogical transformations in iron bearing minerals occurring during thermal treatment at the various roasting temperature intervals, different samples have been subjected to X-ray diffraction analysis. In view to accomplish this, a representative sample from the concentrate has been taken by a riffle divider and a 5 % mixture with coke ground to 35 % - 0.425 mm was prepared. The mixture is placed inside five shamot crucibles and heated respectively to 500°C, 600°C, 700°C, 800°C and 900°C for 30 min. The crucibles are covered with steel lids in order to protect the sample from reoxidation. After time elapsing, the crucibles are cooled down to room temperature and from each of them a predetermined amount is delivered to XRD analysis. They were studied by powder X-ray diffraction phase analysis on a DRON-3M diffractometer, with a horizontal goniometer (radius – 192 mm), Bragg-Brentano geometry and cobalt target (Fe-filtered CoK $\alpha$  radiation,  $\lambda = 0.17903$  nm, 40 kV and 25 mA). Particle size distribution of as received and of ground concentrate has been determined using a Malvern Zeta-Sizer laser diffraction analyzer.

## Roasting, separation and leaching procedures

The preliminary orientation tests have shown that during leaching with 0.96 M sulfuric acid at boiling temperature for one hour, about 33 % of the phosphorus can be removed. From Arrhenius equation, it is known that the diffusion intensity is a function of temperature, as per the following relationship:

$$D = D_0 \cdot \exp(-E_A/RT), \quad (1)$$

where, D is the diffusion coefficient,  $D_0$  is the maximum value for the diffusion coefficient,  $E_A$  is the activation energy, R is the gas constant and T temperature in Kelvin.

The practical implication of this relationship is using the heat during roasting for kicking a solid phase reaction, which will further facilitate the leaching process. For this purpose, high alkaline additive is added to the concentrate so that during the thermal process a reaction with acidic  $[\text{PO}_4]^{3-}$  groups to take place. If the mass and the composition of the mixture used for roasting are fixed, the raise in D will depend only on temperature increase which from its side is limited by two main factors: (1) economical - high temperatures require more fuel per ton ore, and (2) technological – mixture fusion and formation of fayalite and olivine deteriorates the subsequent hydrometallurgical processes, as suggested by Kasen (2005).

The samples of the gravity-magnetic concentrate are placed inside shamot crucibles and then delivered to roasting in electric muffle furnace fitted with thermal controller OMRON E5AX. The temperature is increased in a stepwise manner up to roasting temperature of 900°C and is further kept for one-hour ramp. The heating is then switched off, and the sample is cooled down to room temperature.

The wet medium intensity magnetic separation is done inside a laboratory unit with three  $\text{Nd}_2\text{Fe}_{14}\text{B}$  magnets and induction in the immediate vicinity of the glass vessel 0.34 T. The dry magnetic separation has been carried out either in a cross-belt magnetic separator “Jeffrey – Traylor” 13 or using a lab unit high intensity magnetic separator CC WHIMS 3x4L Carpco Inc. The air gap between the edges of the Jones type grooved plates was set to 3 mm. The non-magnetic fraction is transported to the launder below the matrix by light air jet. Magnetic induction was measured by a FM 205 Tesla-meter “Projekt Elektronik GmbH” furnished with transverse probe AS-NTM. Dry electrostatic separation has been carried out in laboratory unit HT “Carpco” Inc., with charging electrode placed 55 mm above the drum.

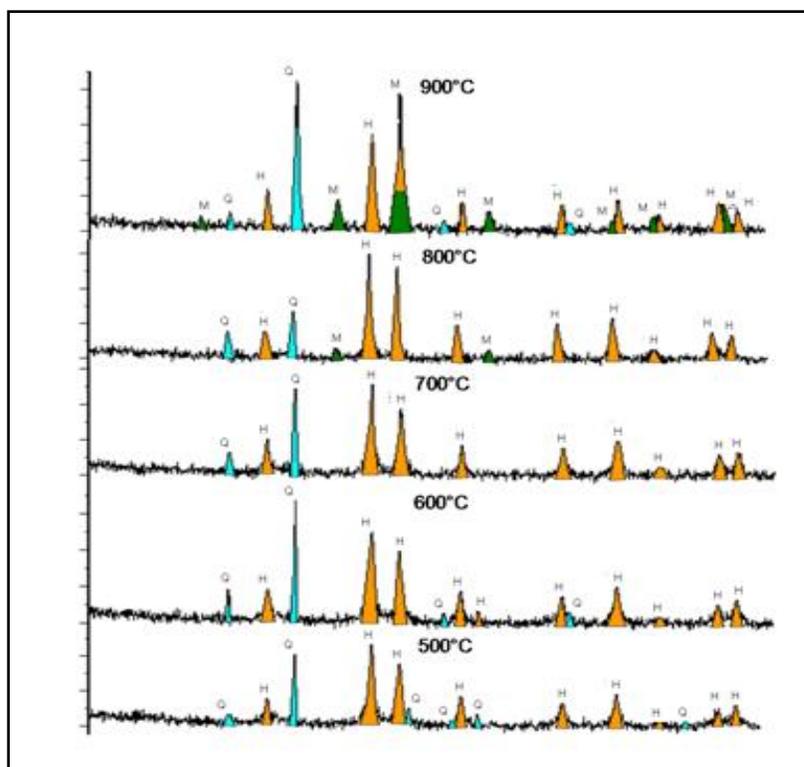
The acid leaching was carried out at 40 % solids (40 grams in 60 ml solution) at ambient temperature inside a mechanically agitated glass reactor. Stirring speed of 450 rpm was kept. Hydrochloric and nitric acids were used as 1M solution, while sulfuric acid as 0.3 M, 0.5 M and 1M. After each test the solid residue was filtered and washed with 200 ml distilled water. For the sulphuric acid leaching, 15, 30, 45, 60 and 120 minute durations were used. All the chemical reagents were of analytical grade (Merck AG, Darmstadt).

## RESULTS AND DISCUSSION

### Mineralogical transformations during roasting of the gravity magnetic concentrate

The results from the XRD analysis of the material are displayed in Figure 1.

The data shown in Figure 1 indicates that peaks of magnetite and maghemite, both being ferromagnetic iron minerals, appear after 800°C, but the transformation is more obvious at 900°C suggesting that more complete reduction takes place at this temperature. At the highest temperature investigated, the number and intensity of peaks corresponding to magnetite/maghemite substantially increase, but the reduction is still not completed because hematite peaks are still present. Quartz remains unchanged since peaks are available within the whole temperature range. The addition of 5 %  $\text{Ca}(\text{OH})_2$  does not provoke any changes in the XRD pattern apart from appearance of  $\text{CaCO}_3$  peaks. It could be argued that lime active substance most probably reacts with  $\text{CO}_2$  from the air. If new mineral species are formed, the intensity of their peaks appears below the background noise due to limonite, which is known as X-ray amorphous.



**Figure 1.** XRD analysis of gravity-magnetic concentrate roasted at temperatures between 500°C and 900°C in reductive media (Q is quartz, H is hematite and M is magnetite/maghemite).

It could be seen that iron content in the samples after roasting increases above 9 % due to limonite dehydroxylation and reduction processes. During roasting, a process resembling boiling is observed, and besides steam and CO<sub>2</sub>, some of the solid constituents are lost in the generated fumes. The other notable change observed is related to quartz, which concentration after roasting is reduced with more than 7 %; phenomena which could be probably attributed to volatile species formation. The principal composition of the concentrate before and after the roasting with coke and lime used additives can be seen in Table 1.

**Table 1.** Chemical and mineralogical composition of the concentrate before and after roasting to maghemite

Concentrate	Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	TiO <sub>2</sub>	MgO	P	Mn	LOI
as received	48.76	12.41	5.93	0.42	0.11	0.42	0.71	0.17	12.31
roasted	58.17	5.17	5.26	3.00	0.29	0.16	0.70	0.22	17 – 19*

\*LOI is for the mixture before roasting

From the analysis shown in Table 1 it could be assumed that the loss on ignition (LOI) is the principle driver leading to chemical composition changes. LOI is increasing from 12.31 without coke and lime addition to 17 to 19 when they were added. Thus, it could be argued that when the maximum roasting temperature is reached, conditions stimulating the volatilization of certain compounds are formed.

## Sulphuric acid leaching of “finely ground” concentrate roasted to maghemite with Ca(OH)<sub>2</sub>

As a rule, when leaching processes are concerned, the smaller material particles, the lower the un-reacted core volume of the material. Therefore, it was assumed that acid leach will be more efficient for a finely ground concentrate. To test this assumption in our case, leaching of a sample ground on dry basis to 80 % - 0,075 mm has been performed. After grinding and drying, it was mixed with 5 % coke and 5 % Ca(OH)<sub>2</sub> and subjected to roasting following the established procedure. The concentrate after roasting acquires red color and ferrimagnetic

properties are induced, indicating that limonite has been transformed to maghemite. Half of the roasted sample was further reground to 95 % - 0,040 mm. For the both samples, ground and re-ground, water leach is carried out at 30 min at 85°C and the material was then subjected to medium intensity magnetic separation likewise shown in the flowsheet in Figure 2.

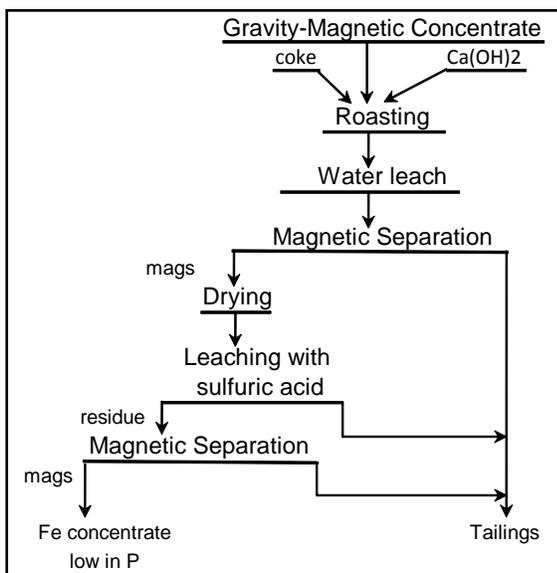


Figure 2. Flowsheet for concentrate roasting and leaching

The wet magnetic separation of the leached pulp has been realized by pouring of the pulp into the beaker of the laboratory separator filled with 600 ml tap water and stirred. The non-magnetic fraction was poured out in a tray, and the magnetic one is washed out. The beaker containing the magnetic fraction is taken away from the magnetic system and discharged in another tray. After drying, weighing and assaying, the mass yield of the magnetic fraction for the “ground to 0.074 mm” sample was in average 69.70 % and that of the “reground to 0.040 mm” sample - 52.80 %. The two concentrates thus obtained were characterized by the following iron and phosphorous concentrations - 58.13 % Fe; 0.47 % P and 56.36 % Fe; 0.49 % P.

Figure 3 presents the dephosphorisation results from the sulfuric acid leaching of the magnetic fraction as shown in Figure 2. The influence of acid concentration, leaching, and the degree of grinding on the level of phosphorous removal has been followed.

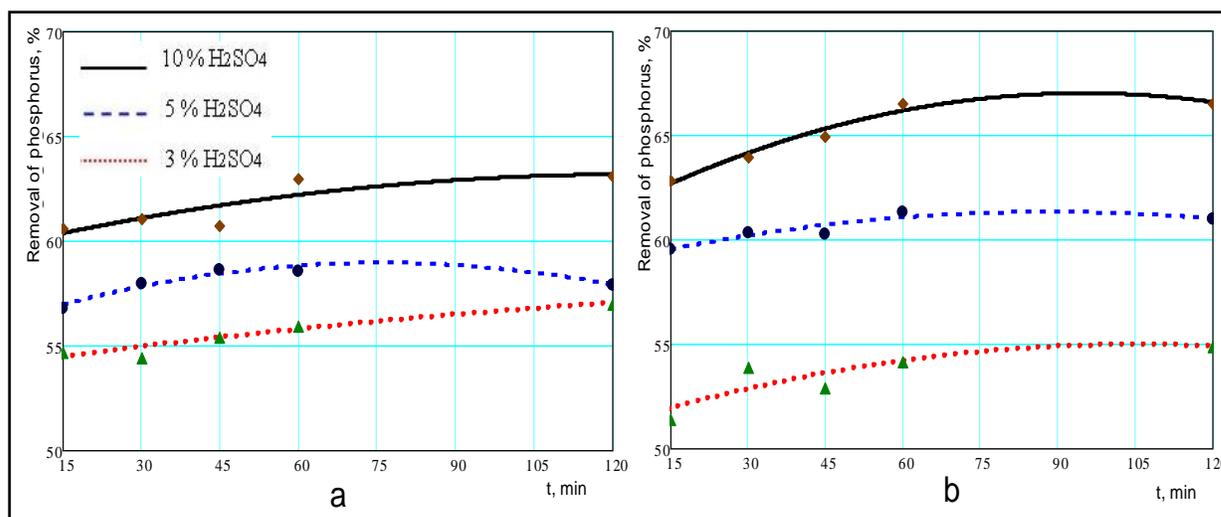


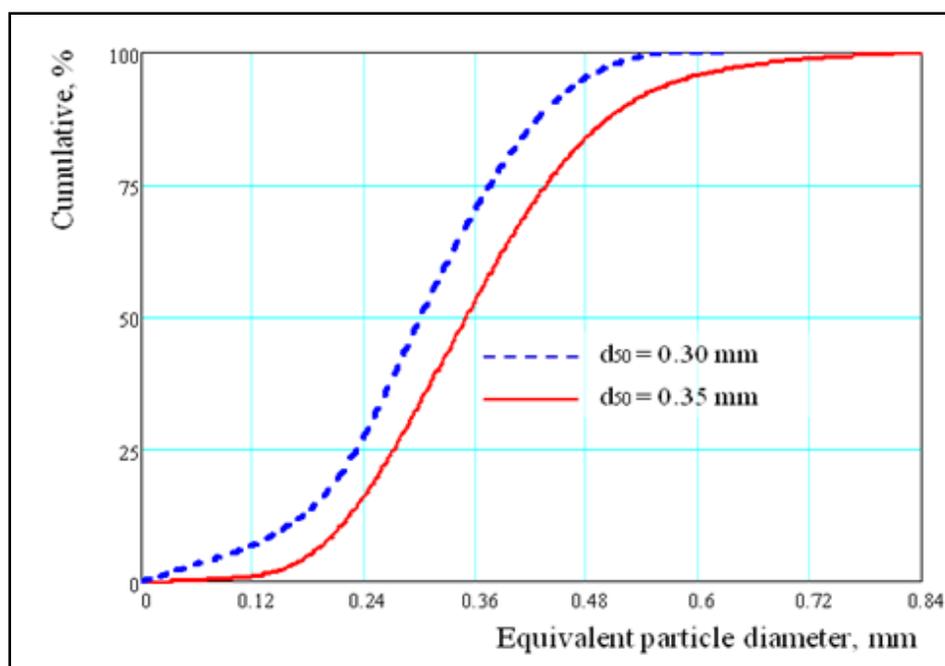
Figure 3. Sulfuric acid leaching of magnetic fractions ground to: a) 80 % - 0.075 mm and b) 95% - 0.040 mm.

The perusal of the leaching curve trends shown in Figure 3 suggests that with increase in acid concentration, the level of phosphorus removal raises as well. Hence, acid concentration becomes a factor of primary importance when dephosphorisation of the investigated concentrate is concerned. It should be noted that one hour leaching has been found sufficient in most of the cases, since no notable difference in the chemical composition of the leach residues after 60 and 120 minutes has been detected. The assays of the leached residues taken after the different durations have shown that it is possible to obtain a dephosphorized concentrate with Fe content from 58.41 to 60.57 % and P – from 0.26 to 0.21 % P for the “ground to 0.074 mm” material. The grade of the iron concentrate obtained from the “ground to 0.04 mm” material has been found to be between 60.12 to 62.03 % Fe and 0.28 to 0.20 % P. These figures are suggesting that the re-grinding improves the dephosphorisation levels from 63 to 67 %, but on the expense of substantial loss in iron.

The results described above have shown that the losses in iron recovery were the main drawback when leaching finely ground sample, but it should be noted that apart from that, wet magnetic separation does not appear quite suitable when acidic pulps are to be handled at industrial scale. The filterability of gypsum is an issue to be considered as well in view process up-scaling. In some studies a preference on hydrochloric and nitric acids is given in this regard, Forssberg and Adolfsson(1981), Muhammed and Zang (1989).

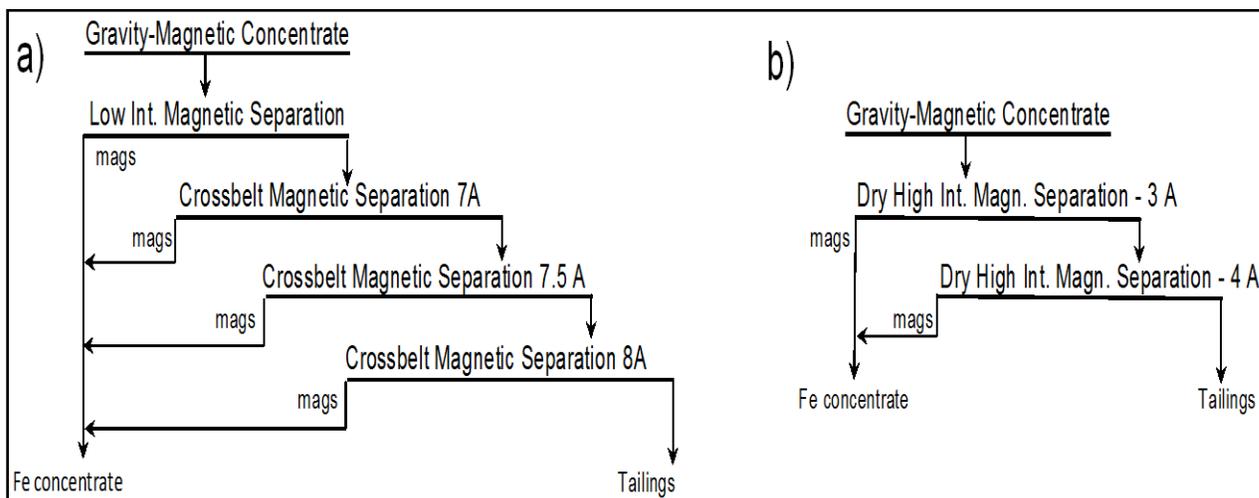
### Hydrochloric and nitric acid leaching of an as received and of “coarsely ground” concentrate roasted with CaO subjected to preliminary and post separation

The optical observations of the oolites have shown that their nuclei's are to a great extent composed of quartz particles. In order to study the effect of a “coarse grind” on the degree of dephosphorisation, a sample from the concentrate has been subjected to grinding in a rotary hammer mill. The particle size distribution for the both samples, the as received concentrate and the grounded one are displayed in Figure 4. It could be seen, that as a result of the “coarse grinding”, the mean particle diameter of the material drops from 0.35 down to 0.30 mm. Although a slight one, this shift in particle size distribution could have a positive effect on the degree of dephosphorization by leaching because of the higher liberation degree e.



**Figure 4.** Cumulative PSD of an as received concentrate ( $d_{50} \sim 0.35$  mm) and of “coarsely ground” one ( $d_{50} \sim 0.30$  mm)

As a general rule, when mineral processing schemes encompass high temperature steps, dry separation routes are preferred. Therefore, for these series of tests, before subjected to roasting with CaO, the concentrate has been processed via a series of dry magnetic pre-separation stages arranged in different combinations shown in Figure 5.



**Figure 5.** Pre-separation routes of the concentrate before roasting: a) cross-belt magnetic separation and b) dry high intensity magnetic separation

As could be seen in Figure 5a, the cross-belt separation involves a rougher and two scavenging magnetic separations aimed at maximizing iron recovery. The rougher operation is carried out at 0.9 T corresponding to a magnetization current of 7 A, the first scavenger at 1.05 T and the second one at 1.13 T. The flowsheet for the dry HIMS (refer Figure 5b) is a simple one, involving one rougher and one scavenger stages. At magnetizing current of 3 A, the induction in the air gap has been measured as 0.567 T, while at 4 A as 0.704 T respectively.

For comparative purposes and in order to evaluate more completely the influence of gangue minerals pre-separation on the leaching efficiency, the two “non-treated” inputs were subjected to leaching as well. As a result, five input samples listed below were prepared for the leaching tests:

- Magnetic fraction from cross-belt separation of an as received GM concentrate – Figure 5 a;
- Magnetic fraction from cross-belt separation of “coarse ground” GM concentrate – Figure 5 a;
- Magnetic fraction from HIMS of “coarse ground” GM concentrate – Figure 5 b;
- An “as received” GM concentrate with d50 ca. 0.35 mm;
- A “coarse ground” GM concentrate with d50 ca. 0.30 mm.

Apart from gangue minerals removal, the other aim of introducing magnetic separation before roasting was to enhance dephosphorisation efficiency by increasing the iron bearing minerals/additive ratio. The five samples mentioned above were at this case roasted with 3 % CaO at 900°C for one hour. As a difference to the preceding tests where the amount of additive was calculated to be in excess to phosphorus but still below the stoichiometrical sum of oxides with acidic properties, in these batches, calcium was added in a 20 % lower amount. This lower dose level was chosen explicitly in order to prevent possible losses of iron during the beneficiation stages. The concern about such losses originates in the fact that during roasting, coatings are formed and fine CaO particles could stick firmly to oolites surface forming iron bearing minerals.

After roasting, all gangue and calcium bearing minerals should be removed to a much possible extent; otherwise, the high alkalinity will provoke increased acid consumption, rendering the process non-efficient. Therefore, to minimize acid consumption in leaching, dry electrostatic and high-intensity magnetic separations have been applied for the five roasted samples following the sequence shown in Figure 6. For the electrostatic separation of the different samples, various parameters of the electric field were used. The three magnetic fractions (samples 1-3) were separated at electric field tension on the main electrode of 25 kV and of 5 kV on the supplementary one.

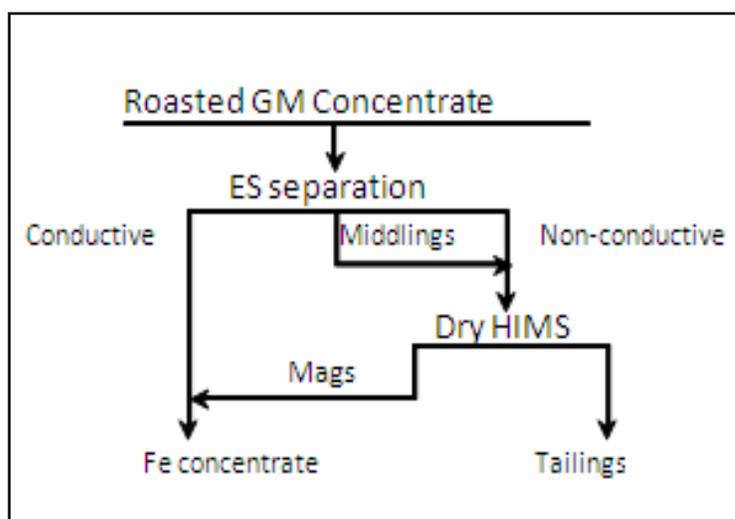
The two rest samples, i.e. samples 4 and 5, were separated at 30 kV, since here the mass of non-conductive particles is substantially higher. The dry HIMS has been carried out in a manner similar to the one described already, using a magnetic field induction of 0.704 T.

Table 2 summarizes the results from the pre-treatment magnetic separations of the concentrate prior to its roasting performed according to the flowsheets in Figure 5.

**Table 2.** Effect of dry magnetic separation of the concentrate prior to roasting

Operation	Product	Mass %	Content		Distribution	
			Fe, %	P, %	Fe, %	P, %
Crossbelt	Feed	100,00	49,57	0,686		
Magnetic	Mags 1	83,11	52,49	0,749	88,00	90,79
Separation	Non-magnetics	16,89	35,21	0,372	12,00	9,17
Crossbelt MS	Feed	100,00	49,71	0,685		
of ground	Mags 2	77,20	51,98	0,742	80,73	83,62
GM concentrate	Non-magnetics	22,80	42,02	0,492	19,27	16,38
Dry High Intensity	Feed	100,00	49,03	0,654		
Magnetic	Mags 3	93,52	51,23	0,679	97,72	97,05
Separation	Non-magnetics	6,48	17,27	0,298	2,28	2,95

Since the ore subject of our study is considered as a high-phos oolitic type limonite and P is mainly included as solid solution, it was expected that the magnetic fractions will be enriched in phosphorus, with its recovery being equal or even higher to that of iron, Ionkov *et al* (2011). This is exactly the situation documented in Table 2. The maximum recovery of iron was achieved in the case of the dry HIMS. Concerning cross-belt magnetic separation, a better grade and higher iron recovery in the magnetic fraction was obtained in the case of the “coarse” concentrate – feed sample 4. Due to the high alkalinity of the mixture in the crucible and the high diffusion coefficient at the temperature ramp used, substantial part of the phosphorus could be driven out from the core of the oolites and report in the structure of the coating, the latter being acid soluble. Moreover, dehydroxilation reactions are valid not only for the goethite but for all clay minerals like chlorite, kaolinite which also release water from their crystal lattices and become more amenable to reaction when CaO is added. The dehydroxilation effects of goethite are investigated in sufficient details by O’Connor *et al* (2006).



**Figure 6.** Pre-treatment flowsheet of the roasted samples before leaching

As mentioned above, after roasting and before leaching, the five products were subjected to electrostatic and dry HIMS sequence as shown in Figure 6. The recovered and enriched in iron concentrate was further subjected to hydrochloric and nitric acid leaching for 5, 10, 15, 30, and 60 minutes. In all the tests, the pulp was kept at 40 % solids density, the acid concentration was 1 M and the stirring speed - 450 rpm. Table 3 displays the leaching results coming only from the 60 minute tests, which are expressed in terms of phosphorous removal degree and feed and leached residue chemical compositions. The results from the complete set of tests (durations 5 – 60 minutes) are displayed in graphical form in Figures 7 and 8. Samples numbering (1 to 5) denotes the leaching feeds using the same convention mentioned in the previous paragraph.

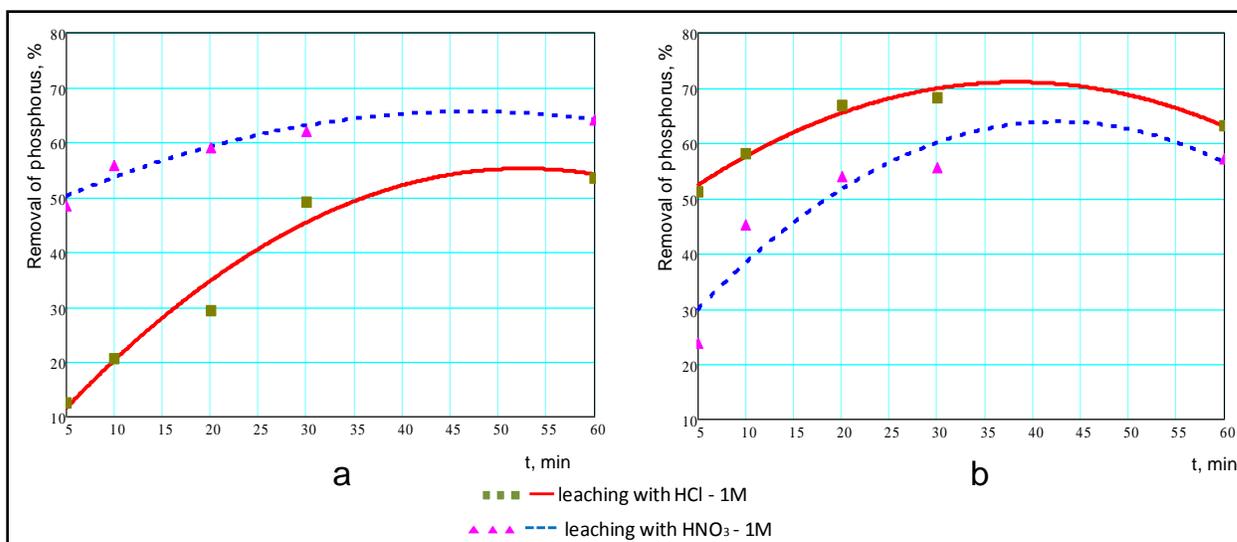
**Table 3.** Comparative hydrochloric and nitric acid leaching of roasted with CaO concentrate subjected to different pre-treatment stages (leaching duration 60 minutes)

Product	Mass, %	Assay, wt %							P removal, %
		Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	P	CaO	MnO	MgO	
Sample 1	100,00	60,44	4,45	5,34	0,47	1,17	0,30	0,20	
Residue / HCl	96,10	62,24	4,28	4,55	0,18	0,18	0,27	0,17	63,98
Residue / HNO <sub>3</sub>	95,90	62,05	4,89	4,43	0,21	0,18	0,27	0,14	56,80
Sample 2	100,00	59,35	3,99	5,48	0,47	1,28	0,30	0,25	
Residue / HCl	96,08	61,33	3,89	4,71	0,18	0,20	0,28	0,16	62,04
Residue / HNO <sub>3</sub>	95,80	61,17	3,96	4,57	0,18	0,27	0,28	0,14	63,23
Sample 3	100,00	58,40	5,81	5,48	0,46	1,49	0,28	0,25	
Residue / HCl	95,75	59,54	5,68	4,66	0,16	0,23	0,27	0,15	66,40
Residue / HNO <sub>3</sub>	95,83	60,20	5,98	4,50	0,16	0,23	0,28	0,12	66,69
Sample 4	100,00	57,47	6,95	5,47	0,46	1,23	0,29	0,25	
Residue / HCl	96,95	58,50	7,54	4,50	0,22	0,20	0,27	0,16	53,95
Residue / HNO <sub>3</sub>	96,98	59,06	7,72	4,60	0,17	0,17	0,27	0,14	64,22
Sample 5	100,00	57,14	8,25	5,30	0,46	1,23	0,28	0,22	
Residue / HCl	96,23	59,07	8,53	4,42	0,16	0,18	0,27	0,15	66,99
Residue / HNO <sub>3</sub>	96,40	59,03	8,29	4,47	0,15	0,19	0,27	0,14	67,68

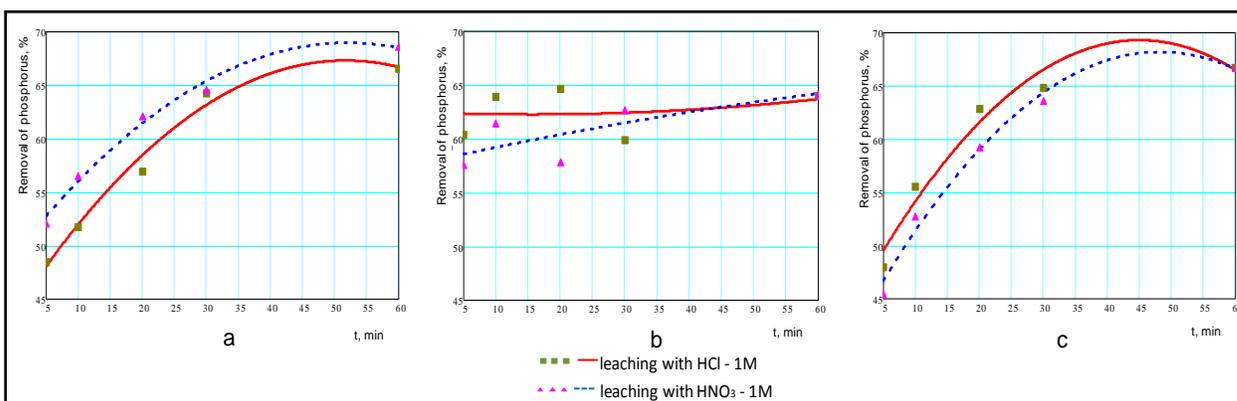
The results for the ground samples (2, 3, and 5) indicate iron losses in the range of 1 to 2 % in the residue after leaching and phosphorus reduction from 0.46 to 0.15 – 0.18 %. In the non-ground samples, phosphorous content is dropped down to 0.17 - 0.22 % depending on the type of acid used.

The dry magnetic separation used as a pre-treatment step before roasting has reflected positively on the grade of the final product. However, for the dephosphorisation degree, the factor with more significant influence was the mean particle size of material. The highest iron grade in the leached concentrate was obtained with sample 1, which is the magnetic fraction of the as received GM concentrate. The application of dry HIMS before roasting reflected in maximizing iron recovery and in minimizing phosphorus content in the leached residues dropping it down to 0.16 % (sample 3).

Concerning SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, the perusal of the data indicates that both acids do dissolve to a certain degree the aluminosilicate minerals. Logically, the component attacked most profoundly by the acids is the CaO – about 85 % dissolution degree. The degree of phosphorus removal is from 54 to 68 %. The amount of dissolved MnO correlates well with the dissolved mass for each respective sample, which suggests that concerning this oxide, leaching is not selective. The MgO is a minor component, which is dissolved from 18 to 54 %, most probably due to its inclusions in clay minerals. The phosphorous removal for most of the tested samples follows a parabolic trend as could be seen in Figures 7 and 8 below.



**Figure 7.** Leaching of an as received non-ground samples: a) sample 4; b) sample 1



**Figure 8.** Leaching of “coarsely ground” samples: a) sample 5; b) sample 2 and c) sample 3

It could be argued, that the nitric acid shows better dephosphorisation efficiency for the concentrate roasted without preliminary removal of gangue minerals. The leaching results for the as received “non-ground” sample (No 4) indicate that phosphorous removal degree steadily increases with leach duration. For sample 1, an optimal leaching duration of around 30 minutes could be detected. The P removal trend with hydrochloric acid shown in Figures 7b and 8b suggests slight loss in efficiency after the first half an hour and up to 60 minutes. This observation could be a sign for phosphorus precipitation at the vacant places of the hematite crystal lattice, a phenomena already reported by others, Foerster (1941), Zhang and Muhammed (1989).

The hydrochloric acid shows higher efficiency for the samples pre-treated by magnetic separation before roasting. If this operation is not included, than nitric acid is a better option. The observed differences between both acids in terms of dephosphorisation efficiency are less pronounced for the “coarsely ground” material than for those of the “as received” one. In this context, it should be reminded that the difference in mean particle size for the two feeds was only 0.05 mm.

## CONCLUSION

The presented and discussed above results offer the possibility the following conclusions to be drawn:

If phosphorus concentration in the studied material has to be dropped down to 0.15 – 0.20 % via acid leaching than only roasting to hematite seems sufficient step. Fine grinding of material down to 80 % - 0.075 mm or to 95 % - 0.040 mm does not seem beneficial in view dephosphorisation efficiency improvement.

When an alkaline earth additive is used in roasting, higher efficiency of P removal is achieved with nitric and hydrochloric acids, both when “as received” or “coarse ground” concentrates were used.

Nitric acid has been more efficient than the hydrochloric one in removal of phosphorus from sample non-beneficiated before roasting, regardless the particle size of the input material.

During one hour acid leaching, the degree of phosphorus removal has varied between 54 and 67.7 % based on the pre-treatment steps and the acids used.

The best phosphorus removal was achieved with “coarse ground” material, suggesting that particle size distribution is a technological factor worth to be considered. The hydrochloric acid has shown higher leaching efficiency than the nitric one for the enriched in iron concentrates samples (No 1 – 3). The gangue minerals separation prior to roasting reflects favorably on the recovery of iron in the final product.

Maximum removal of phosphorus at maximum iron recovery could be achieved by “coarse” grinding of the concentrate, followed by dry HIMS for removal of gangue minerals, roasting at the optimally found conditions and leaching with 1 M hydrochloric acid.

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## REFERENCES

- Akatov, A I, Lyashchenko, A G, and Toptalova, I N, 1969, Clarification of the possibility of removing phosphorus from Lisakovkii ore concentrate, *Obogashchenie Rud* 14(3):47, Chemical Abstracts, 1970, topic No 9-66-198b.
- Belikov, V V, Ogorodov, V B, Jadrishnikov, A O, Mikhailovna, N A, Chop, and S V, 2002, Method for Cleaning of Iron Ore Concentrate from Phosphor Contaminants, RU Patent No RU2184158.
- Belikov, V V, Ogorodov, V B, Yadrishnikov, A O, and Mihailovina, N A, 2003, Obesphosphorivanie Burojeleznyakovih Rud I Kontzentratov, *Obogashchenie Rud No 3*, pp 8 – 12.
- Edwards, C I, Fisher-White, M J, Lovel, R R, and Sparrow, G J, 2011, Removal of Phosphorus from Australian iron Ores, *Iron Ore 2011*, Perth, Australia, pp 403 – 412.
- Feld, I L, Franklin, T W and Lampkin, W M, 1966, Process for removing phosphorus from iron ores. United States Patent No 3402041.
- Fisher-White, M J, Lovel, R R, Sparrow, G J, 2009. Phosphorus Removal from Iron Ore with a Low Temperature Heat Treatment, *Iron Ore 2009*, Perth, WA, pp 249 – 254.
- Foerster, C V, 1941, Removal of phosphorus from ores, US Patent No 2, pp 238 586.
- Forsberg, E, Adolfson, G, 1981, Entphosphorung von hochphosphorhaltigen Eisenerzen durch saure Laugung, *Erzmetall* 34, Nr. 6, pp 316 – 322.
- Gooden, J E A, Walker, W M, Potts, A E and Heinzle, U A, 1973, Process for the reduction of phosphorus content of iron ores, Australian Patent 457026, 17 May 1973.
- Gooden, J E A, Walker, W M, Allen, R J, 1974, “AMDEPHOS”- A chemical process for dephosphorisation of iron ore, *Proceedings of National Chemical Engineering Conference*, Queensland, pp 21 – 33.

- Ionkov, K, Gaydardzhiev, S, Correa de Araujo, A, Kokal, H, Pirson, A, 2011, Dephosphorisation of Limonitic Iron Concentrate by Roasting, Acid Leaching and Magnetic Separation, *Iron Ore 2011*, Perth, Australia, pp 445 – 452.
- Khasen, B P, 2005, Problemi ispolzovania burojelyakovih rud Lisakovskovo mestorojdeniya, *Izvestia visshih uchebnih zavedenii*, *Chernaya Metalurgia* 3, pp 8 – 10.
- Kokal, H R, Farias, J M, 2008, A Roasting – Leaching Demonstration Plant for Removal of Phosphorus from Iron Ore, *Hydrometallurgy 2008: Proceedings of the Sixth Int. Symposium*, pp 431 – 438.
- Kossava, V P, Nevoysa, G G, Komarova, N E, Mamicheva, V P, 1996, Mineralogicheskie I Teksturno-Strukturnyye Osobnosti Kimmeriyskikh Zheleznyh Rud Severnogo Priazov'ya, rus. *Geologiya Rudnykh Mestorozhdeniy*, 1966 Vol. 8, Issue 1, Rossiyskaya Akademya Nauk: Moscau, pp 83 – 92.
- Muhammed, M and Zang, Y, 1989, A hydrometallurgical process for dephosphorization of iron ore, *Hydrometallurgy*, 21: pp 277 – 292.
- O'Connor, F, Cheung, W H, Valix, M, 2006, Reduction roasting of limonite ores: effect of dehydroxilation, *International Journal of Mineral Processing*, 80, pp 88 – 99.
- Zhang, Yu and Muhammed, M, 1989, The Removal of Phosphorus from Iron Ore by Leaching with Nitric Acid, *Hydrometallurgy*, 21, pp 255 – 275.
- Zhu, D, Xiao, Y, Chun, T, Chen, B and Pan, J, 2010, Upgrading and removing phosphorus from low-grade and high-phosphorus containing iron ores, XXV International Mineral Processing Congress, The Australasian Institute for Mining and Metallurgy: Melbourne, pp 1667 – 1676.