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DEPHOSPHORIZATION OF OXIDIZED IRON ORE FROM GARA DJEBILET, TINDOUF (ALGERIA)

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ДЕФОСФОРИЗАЦІЯ ОКИСЛЕНОЇ ЗАЛІЗНОЇ РУДИ РОДОВИЩА ГАРА ДЖЕБІЛЕТ, ТІНДУФ (АЛЖИР)

Purpose. The study of this scientific work concerns the treatment of the oolitic iron ore deposit of Gara Djebilet, Tindouf, Algeria. Chemical and mineralogical analyzes performed on the representative sample taken from the studied area show high presence of phosphorus oxide P_2O_5. This negatively affects the quality of iron and steel products. Quality improvement and reducing the content of impurities in the studied iron ore were the main objectives of the present research study.

Methodology. To identify this ore, characterization is carried out on polished sections and thin blades, as well as a chemical analysis of the initial sample, an XRD analysis of different size fractions of the initial sample, a chemical analysis of major elements of iron ore from Gara Djebilet by XRF and quantitative analyses by EDX 74. Tests are conducted on different types of roast slices with grain sizes of (-0250 + 0.125; -0.125 + 0.063; 0.045 + -0063 and -0045 + 0.00) mm. Calcium chloride $CaCl_2$ additional to the dose ratio with iron ore: 10:90, 15:85, 20:80, 25:75 at different temperatures, 600 ºC, 700, 800 and 900 ºC. After cooling, the roasted mass is analyzed with XRF.

Findings. Different size fractions of the crude sample were analyzed by XRD. The obtained results show that the mineralogical composition comprises: hematite, phosphorus, silica, alumina and lime. The best results are achieved with the following parameters: the particle size range - 0.063 + 0.045 mm, upon the complete release of the useful component of its matrix with a P_2O_5 content equal to 0.06 % and Fe_2O_3 equal to 61.67 %. The effect of $CaCl_2$ (alkaline earth metal additive) on phosphorus during the roasting of iron ore in the ratio of 20 % $CaCl_2$ and 80 % Fe_2O_3 contributes greatly to the reduction of phosphorus in the ore from Gara Djebilet, Tindouf, Algeria.

Originality. The Gara Djebilet iron deposit has not been exploited yet due to its high phosphorus content. The originality of this research work resides in the application of the roasting process using calcium chloride at different grain sizes, temperatures and concentrations.

Practical value. This method allows us to reduce the phosphorus to an acceptable level for the steel industry. The present process is simple, economical and does not require investment in industrial equipment.

Keywords: *iron ore, Gara Djebilet, dephosphorization, roasting, calcium chloride*

Introduction. The oolitic iron ore of the Gara Djebilet deposit is not considered as a commercial product due to its high phosphorus content.The objective of the study is to reduce the phosphorus content and increase the iron content in order to meet the steel industry requirements. Research works are carried out on oolitic iron ores of high phosphorus content. Several articles have been published in various international journals. Ionkov (2012, 2013) subjected the oolitic iron ore to 900 ˚C for one hour. The application of leaching, physical separation and salts washing resulted in a phosphorus reduction of 0.7 to 0.15 %. A study on the potential of micrococcus species to remove phosphorus (P) from Nigeria's Agbaja iron ore was carried out by submerged culture technique by O. W. Obot (2012).Obiorah S.M.O. et al. (2011) conducted a research study on the effects of residence time, dilution rate, leachate concentration, and the interaction of variables on dephosphorization of Agbaja iron ore. They used the chemical leaching technique [H_2SO_4] and 23-factorial surface response methodology. The goethitic fraction can be removed with a heating pretreatment of about 300 °C for 1 h followed by caustic leaching. The direct reduction technology by the addition of sodium carbonate (Na_2CO_3) and magnetic separation was developed by Zhu, D. Q. et al. (2013) to treat high-phosphorus iron ore from Western Australia. According to Yang, M. et al. (2015), the results indicate that the phosphorus in the mineral is associated with goethite and exists mainly in the Fe_3PO_7 amorphous phase. The phosphorus remains in the amorphous phase after having been roasted below 300 °C. Li, Y. L et al. (2012), obtained the best results for the removal of phosphorus in direct-reduction roasting from Ningxiang-type high-phosphorus oolitic hematite, provided that the dephosphorizing agent NCP and the new dephosphorizing agent TS are used together. A better rate of recovery was obtained by direct reduction roasting with dephosphorization agent followed by two steps of crushing and magnetic separation by XU, C. Y. et al. (2012). The P content decreases by 0.82 % in the crude ore and 0.06 % in the concentrate. A new method (based on gas separation plus melt separation) was proposed by Tang, H. Q. et al. (2010) to remove phosphorus from iron ore with a high phosphorus content, in which phosphorus content was 1.25 and 50.0 % iron content.

Identification of the deposit. Location and reserves. The Gara Djebilet iron deposit is located in the south-west of the Tindouf basin, 130 km south-east of the town of Tindouf, near the Algerian-Mauritanian border, as shown in Fig. 1. The studied mine is in the exploration phase and has not entered production yet. Three main separate deposits have been recognized throughout the East-West region extending over approximately 60 km. The exploitable reserves of Gara Djebilet are around 1.7 billion tons at 57 % of iron, located in two important lenses: the so-called "West" lens with 780 million tons and the called "center" lens with 900 million tons (Bersi et al., 2016).

Ore characterization. Observation in polished sections. The observation of the polished sections shows primary minerals representing roundish-grained magnetite at 0.2 mm of brownish color (Fig. 2, *a*). Hematite forms the fouling structure around the magnetite grains (Figs. 2, *b, c*).The presence of goethite – hydro-goethite

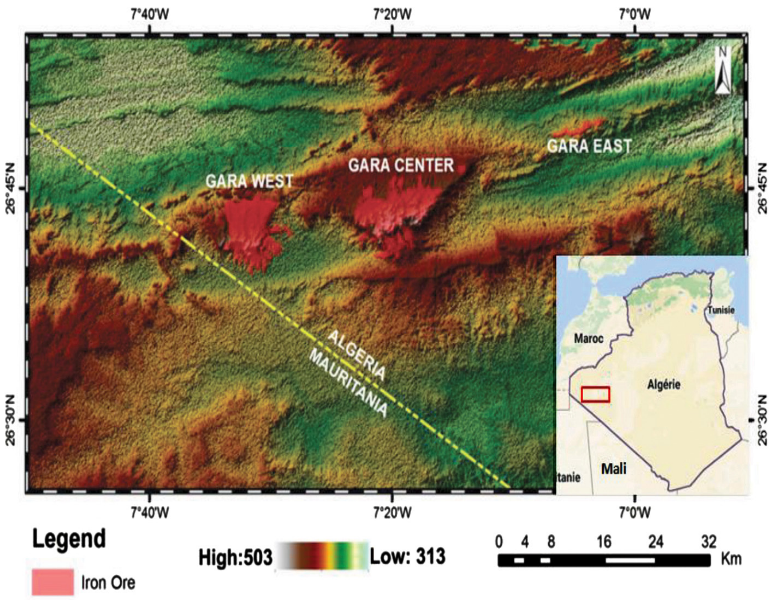


Fig. 1. Geographical location of the Gara Djebilet deposit (Bersi et al., 2016)

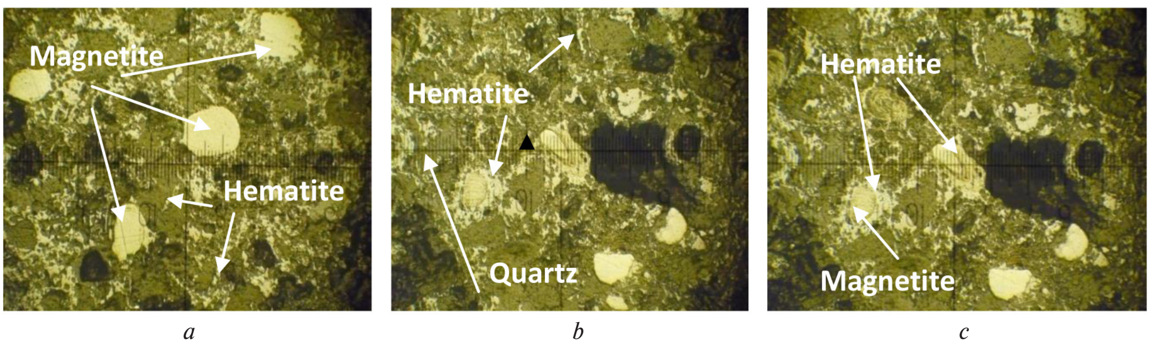


Fig. 2. Original minerals:

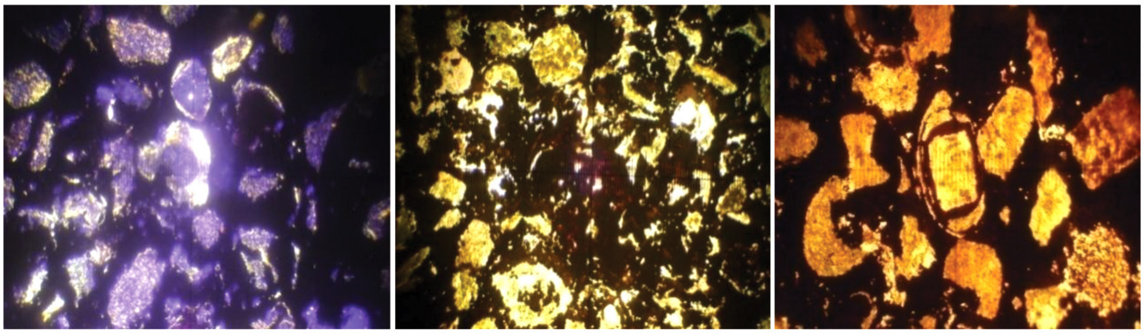
a – grains of magnetite and aggregates of hematite between grains of non-metallic minerals; b – rims of hematite around grains of quartz and magnetite; c – magnetite with rims of hematite in the intergranular space of ore in which magnetite grains is 3.2 %, hematite 5–10 % and goethite-hydrogoethite 20–25 %.

The structure is composed of rounded grains of clay minerals. Sometimes the grains have a clear zonal structure (Fig. 3, *a*).The nonmetallic components of the ore grains are cemented and shine in a light reddish brown space (Fig. 3, *b*). Often, non-metallic grains are observed in the central part composed of a clay material, this part is surrounded by a border of the metallic unit of the ore and mineral chlorite (Fig. 3, *c*).The ore rate (metal unit) is of the order of 45–50 %, while the non-metallic unit consists of 50 to 65 % of the mass of the rock.

Characterization of Gara Djebilet iron ore by X-ray fluorescence. The chemical analysis of the initial sample was carried out at the research laboratory of the SOMIPHOS-El Hadjar steel complex, Annaba, Algeria. The obtained results are shown in Table 1.

The results show that the ore is relatively rich, while the phosphorus content is high, 1.89 % of P_2O_5. The particle size analysis is performed in the laboratory of Development of Mining Resources and Environment of the University of Badji Mokhtar, Annaba, Algeria. The samples were screened with a series of different mesh sieves. The particle size analysis should separate the grains of the ore and classify them by diameter. In order to provide this study with more information about the sample to be studied, a chemical particle size analysis is carried out at the Laboratory of the National Office of Geological and Mining Research of Boumerdes, Algeria. The results of analysis of the various size fractions of the major elements, Fe_2O_3 and P_2O_5 by X-ray fluorescence are presented in Table 2.

Characterization of the initial sample by XRD. The taken sample were finely crushed and then analyzed by X-ray diffraction (XRD). The obtained spectra are composed of several peaks, corresponding to the mineralogical composition. The results obtained relating to diffraction spectra X-ray of the original sample, are shown in Fig. 4.



a *b* *c*

Fig. 3. The structure of minerals:
a – zonal structure of clay minerals; b – non-metallic components (central part) in the cement matrix; c – grains of clay minerals, surrounded by a border of the ore mineral and chlorite

Table 1

Results of chemical analysis of iron ore from Gara Djebilet by X-ray fluorescence

Element	Fe_2O_3	SiO_2	CaO	Al_2O_3	MgO	MnO	P_2O_5	SO_3	K_2O	Na_2O	PAF
Component (%)	57.00	5.92	4.68	3.97	1.42	1.28	1.89	1.07	0.48	0.19	9.86

Table 2

Results of particle size analysis of the major elements of the iron ore from Gara Djebilet by X-ray fluorescence

Size fractions, (mm)	Yield, (%)	Cumulative refusal, (%)	Cumulative passers, (%)	Iron content, (%)	Content P_2O_5 (%)
+2	53.65	53.65	100	59.62	1.76
-2 + 1	13.96	67.61	46.35	56.18	1.63
-1 + 0.5	10.91	78.52	32.39	60.70	1.92
-0.5 + 0.25	06.41	84.93	21.48	57.04	1.80
-0.25 + 0.125	06.56	91.49	15.07	57.81	1.74
-0.125 + 0.063	06.02	97.51	08.51	61.09	1.97
-0.063 + 0.045	01.04	98.55	02.49	60.82	1.90
-0.045 + 0	01.45	100	01.45	59.57	2.12
Total	100	-	-		

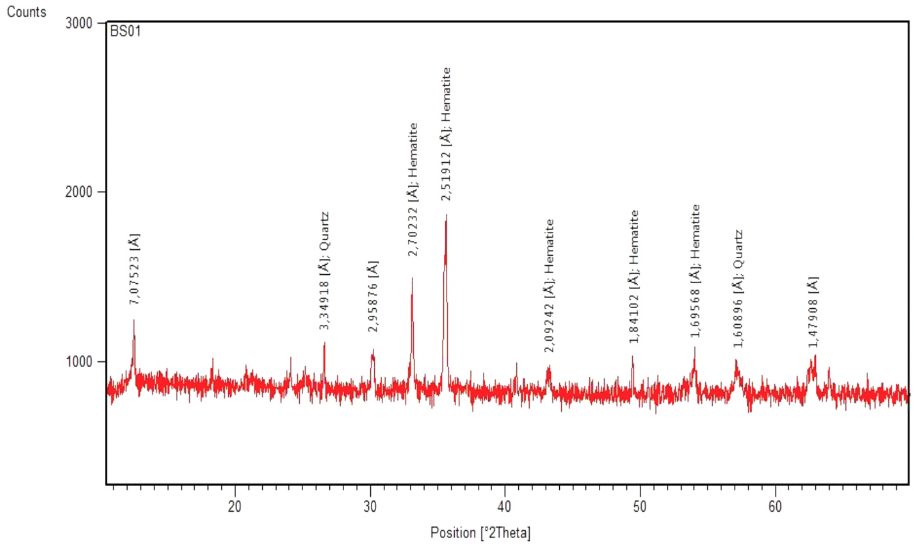


Fig. 4. X-ray diffraction spectrum of the initial sample of iron ore from Gara Djebilet

The XRD shows a mineralogical diversity including: clay, silica, hematite, goethite; since elements with a rate less than 1 % are not detected by the XRD, for this purpose an alternative method of analysis is used.

Sample characterization by SEM. Using a SEM microscope, an image was taken for the iron ore sample from the Gara Djebilet deposit as shown in Fig. 5, with a magnification of 3000 times.

According to Fig. 6, the EDX analysis conducted by SEM of an iron ore sample taken from the Gara Djebilet deposit shows, on the one hand, a large peak of two elements represented by O and Fe. On the other hand, the presence of silica and alumina (Si and Al) indicates the presence of a clay fraction in this iron ore (8 %). The presence of Ca and Mg is reflected by a minimal presence of carbonates (calcite and dolomite). Finally, it is clear on the spectrum that this sample contains phosphorus (probably in the form of apatite) with a rate of P = 0.39 %.

Materials and method. ***Collection and characterization of samples.*** The iron ore samples on which this work is based are collected from different locations in the Gara Djebilet deposit, in order to cover the maximum area of study with an acceptable level of reliability. The iron ore sample is crushed and subjected to chemical analysis using XRF in order to define the chemical composition of the crushed crude iron ore from Gara Djebilet.

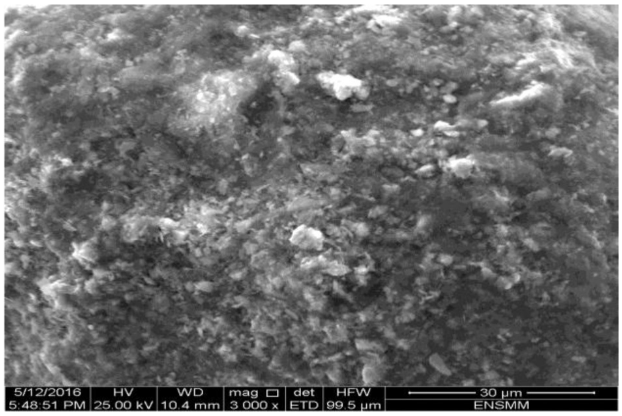


Fig. 5. Observation of Gara Djebilet iron ore by SEM

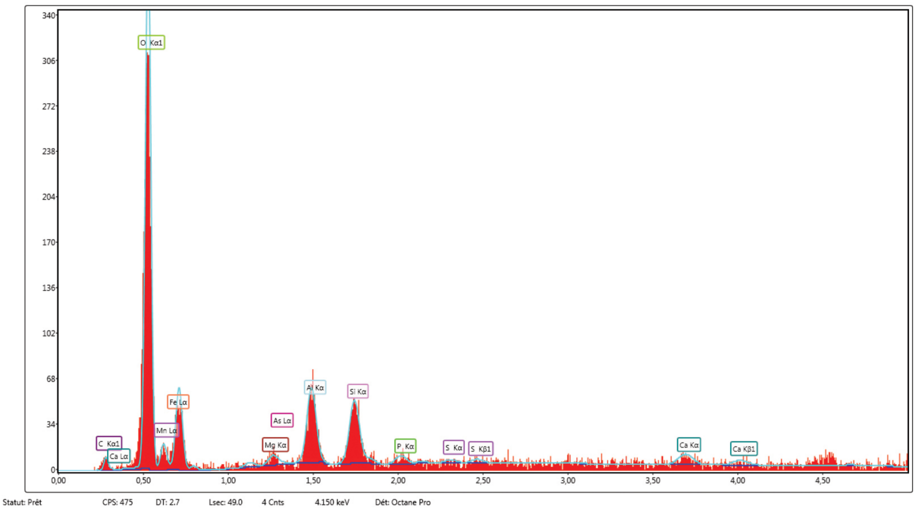


Fig. 6. Quantitative analysis by EDX 74

Roasting of iron ore from Gara Djebilet. Different types of slices were roasted with particle sizes of (-0.250 + 0.125; -0.125 + 0.063; -0.063 + 0.045 and -0.045 + +0.00) mm, adding $CaCl_2$ to the iron ore dose ratio of 10:90, 15:85, 20:80, 25:75 at different temperatures of 600 °C, 700, 800 and 900 °C. After cooling, the roasted mass is analyzed by XRF; the results obtained in Table 3 show the effect of roasting with additive on the iron ore as regards the extent of the dephosphorization.

Effect of particle size distribution on phosphorus reduction. Fig. 7 shows how particle size influences the reduction of phosphorus during roasting. It can be seen from the graph that as the particle size decreases, there is a decrease in phosphorus as well.

Effect of temperature on phosphorus content in iron ore. Fig. 8 shows that the temperature affected the phosphorus during the roasting of the Gara Djebilet iron ore;

Table 3

Results of Gara Djebilet iron ore roasting tests

Particle size classes (mm)	P_2O_5 (%)	Fe_2O_3 (%)	Weight $CaCl_2$ (g)	Weight Fe_2O_3 (g)	Temperature (C°)	P_2O_5 (%)	Fe_2O_3 (%)
-0.250 + 0.125	1.74	57.81	10	90	600	1.56	57.93
					700	1.39	57.97
					800	1.14	58.68
					900	1.03	58.96
-0.125 + 0.063	1.97	61.09	15	85	600	1.18	60.67
					700	1.09	61.84
					800	1.02	61.97
					900	0.97	62.01
-0.063 + 0.045	1.90	60.82	20	80	600	0.29	60.78
					700	0.09	61.19
					800	0.06	61.67
					900	0.13	60.96
-0.045+0.00	2.12	59.57	25	75	600	0.65	59.53
					700	0.48	58.61
					800	0.39	53.39
					900	0.40	53.46

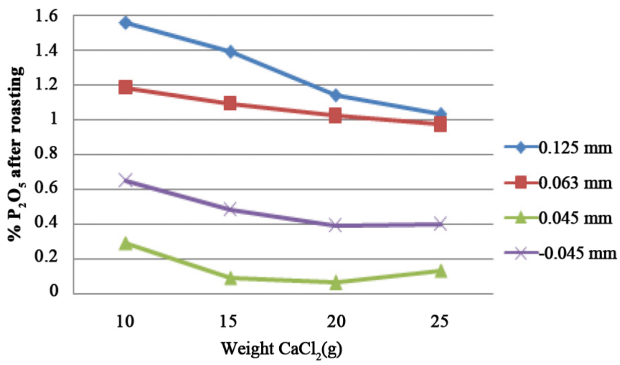


Fig. 7. Effect of granulometry on phosphorus during roasting

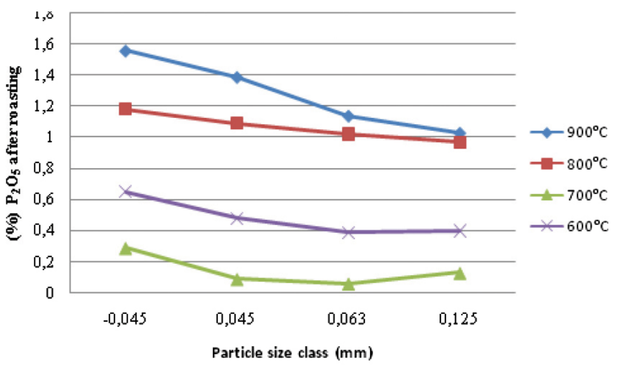


Fig. 8. Effect of temperature on phosphorus during iron ore roasting

the increase in temperature increases the rate of phosphorus removal.

Effect of $CaCl_2$ additive on phosphorus content in iron ore. The calcium chloride is used to roast iron ore from Gara Djebilet; it influenced the phosphorus in the iron ore in the main, as it contributes to the reduction of phosphorus as shown in Fig. 9.

Results and discussion. The effect of the granulometry of the particles as a function of the $CaCl_2$ dosage with respect to the iron ore is studied. It can be seen from Fig. 7 that the decrease in particle size affects the dephosphorization of the iron ore. The best results are achieved for the particle size range of -0.063+ +0.045 mm. The P_2O_5 content reached 0.06 % and that of Fe_2O_3 was 61.67 %, which is consistent with the previ-

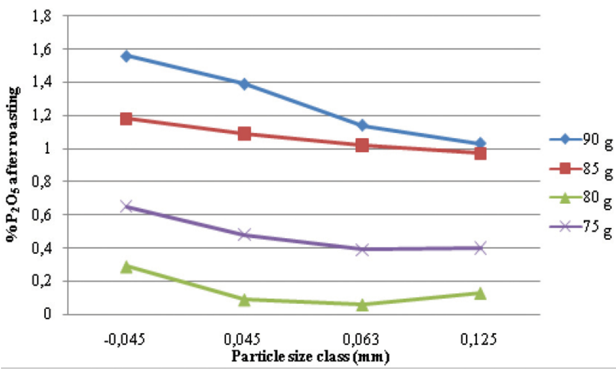


Fig. 9. Effect of $CaCl_2$ (alkaline earth metal additive) on phosphorus during roasting of iron ore

ous work as indicated in the bibliography. Fig. 8 shows that an increase in the temperature from 600 to 900 °C resulted in a phosphorous removal rate in the iron ore. When the temperature is high, good dephosphorization is obtained. The best results are obtained for a granulometry of -0.063 + 0.045 mm, when the useful component of its gangue is completely released with a P_2O_5 content equal to 0.06 % and Fe_2O_3 equal to 61.67 %.The effect of $CaCl_2$ (alkaline earth metal additive) on phosphorus during the roasting of iron ore in the ratio of 20 % $CaCl_2$ and 80 % Fe_2O_3, as shown in Fig. 9, contributes greatly to the reduction of phosphorus in the Ore from Gara Djebilet, Tindouf, Algeria.

Conclusion. In this study, the possibility of using an alkaline earth metal ($CaCl_2$) for a dephosphorization of the iron ore from the Gara Djebilet deposit, with a view to its exploitation. It has been found that the iron ore of this deposit depends on the parameters of the roasting process, such as, particle size, temperature, and oxidizing additive. However, it is proven that the dephosphorization of iron ore from Gara Djebilet depends on the variables process mentioned above and has given very encouraging results.

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Мета. Дослідження даної наукової роботи пов'язані зі збагаченням оолітової залізної руди родовища Гара Джебілет, Тіндуф, Алжир. Хімічні й мінералогічні аналізи, виконані на представницькому зразку, відібраному із досліджуваної області, показують високий вміст оксиду фосфору P_2O_5. Це негативно впливає на якість металургійної продукції. Поліпшення якості шляхом зниження вмісту домішок у дослідженій залізній руді було головною метою представленого дослідження.

Методика. Для ідентифікації даної руди виконано вивчення аншліфів і прозорих шліфів, хімічний аналіз вихідного зразка, рентгеноструктурний аналіз фракцій різної величини з вихідного зразка, хімічний аналіз основних елементів залізної руди з Гара Джебілет за допомогою рентгенодіфракції, кількісні аналізи із застосуванням EDX 74. Тести проводилися на різних типах спечених зрізів із розміром фракції (-0250 + 0.125; -0.125 + 0.063; 0.045 + -0063 і -0045 + 0.00) мм. Хлорид кальцію $CaCl_2$ був доданий до залізної руди у пропорціях: 10:90, 15:85, 20:80, 25:75 за різних температур, відповідно, 600 °C, 700, 800 і 900 °C. Після охолодження спечена маса була проаналізована за допомогою рентгеноструктурного аналізу.

Результати. Було проведено дифракційне дослідження фракцій різної розмірності, узятих із сирих проб. Отримані результати показують, що мінералогічний склад включає в себе гематит, фосфор, кварц, глинозем і вапно. Найбільш оптимальні результати досягнуті при наступних параметрах: діапазон величини частинок -0.063 + 0.045 мм, після повного вивільнення корисного компонента матриці вміст P_2O_5 відповідає 0.06 % при вмісті Fe_2O_3 рівному 61.67 %. Вплив $CaCl_2$ (добавки лужно-земельного металу) на фосфор під час прожарювання залізної руди у відношенні 20 % $CaCl_2$ і 80 % Fe_2O_3 значно сприяє зниженню вмісту фосфору в руді з родовища Гара Джебілет, Тіндуф, Алжир.

Наукова новизна. Родовище залізної руди Гара Джебілет ще не експлуатується через високий вміст фосфору в руді. Оригінальність цієї дослідницької роботи полягає в застосуванні процесу прожарювання з використанням хлористого кальцію різної зернистості, із застосуванням різних температур і різних концентрацій.

Практична значимість. Цей метод дозволяє зменшувати вміст фосфору до рівня, допустимого для металургійної промисловості. Існуючий процес простий, економічний і не вимагає вкладень у промислове обладнання.

Ключові слова: *залізна руда, Гара Джебілет, дефосфоризація, прожарювання, хлорид кальцію*

Цель. Исследования данной научной работы связаны с обогащением оолитовой железной руды месторождения Гара Джебилет, Тиндуф, Алжир. Химические и минералогические анализы, выполненные на представительном образце, отобранном из исследуемой области, показывают высокое содержание оксида фосфора P_2O_5. Это отрицательно влияет на качество металлургической продукции. Улучшение качества путем снижения содержания примесей в исследованной железной руде было главной целью представленного исследования.

Методика. Для идентификации данной руды выполнено изучение аншлифов и прозрачных шлифов, химический анализ исходного образца, рентгеноструктурный анализ фракций различной величины из исходного образца, химический анализ основных элементов железной руды из Гара Джебилет посредством рентгенодифракции, количественные анализы с применением EDX 74. Тесты проводились на различных типах спеченных срезов с размером фракции (-0250 + 0.125; -0.125 + 0.063; 0.045 +-0063 и -0045 + 0.00) мм. Хлорид кальция $CaCl_2$ был добавлен к железной руде в пропорциях: 10:90, 15:85, 20:80, 25:75 при различных температурах, соответственно, 600 °C, 700, 800 и 900 °C. После охлаждения спеченная масса была проанализирована при помощи рентгеноструктурного анализа.

Результаты. Было проведено дифракционное исследование фракций различной размерности, взятых из сырых проб. Полученные результаты показывают, что минералогический состав включает в себя гематит, фосфор, кварц, глинозем и известь. Наиболее оптимальные результаты достигнуты при следующих параметрах: диапазон величины частиц -0.063 + 0.045 мм, после полного высвобождения полезного компонента матрицы содержание P_2O_5 соответствует 0.06 % при содержании Fe_2O_3 равном 61.67 %. Воздействие $CaCl_2$ (добавки щелочноземельного металла) на фосфор во время прокаливания железной руды в отношении 20 % $CaCl_2$ и 80 % Fe_2O_3 значительно способствует снижению содержания фосфора в руде из месторождения Гара Джебилет, Тиндуф, Алжир.

Научная новизна. Месторождение железной руды Гара Джебилет еще не эксплуатируется из-за высокого содержания фосфора в руде. Оригинальность этой исследовательской работы состоит в применении процесса прокаливания с использованием хлористого кальция различной зернистости, с применением различных температур и разных концентраций.

Практическая значимость. Этот метод позволяет уменьшать содержание фосфора до уровня, допустимого для металлургической промышленности. Существующий процесс прост, экономичен и не требует вложений в промышленное оборудование.

Ключевые слова: *железная руда, Гара Джебилет, дефосфоризация, прокаливание, хлорид кальция*

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