

Article

Influence of Hydrofluoric Acid Leaching and Roasting on Mineralogical Phase Transformation of Pyrite in Sulfidic Mine Tailings

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Received: 14 April 2020; Accepted: 26 May 2020; Published: 1 June 2020



Abstract: Under the oxidative roasting process, pyrite, as a major mineral in sulfidic mine tailings, can transform to iron oxides. Generated iron oxides, if exhibiting enough magnetic properties, can be recovered via magnetic separation resulting in partial mine tailings valorization. However, due to the presence of various minerals and sintering possibility, it is advantageous to remove impurities and increase the pyrite content of mine tailings prior to the roasting procedure. In this case, hydrofluoric acid that has no influence on pyrite can be used to leach most inorganic minerals, including aluminosilicates. Therefore, this study investigated and compared the influence of the roasting process with and without hydrofluoric acid leaching pretreatment on mineralogical phase transformation of pyrite and magnetic properties of thermally generated minerals. Several tests and analyses were performed to study mineralogical phase transformation, morphology, elemental composition, surface characterization, and magnetic properties. Results of this study indicated that without acid leaching pretreatment, pyrite was mainly transformed to hematite. However, via acid leaching, fluorine, as a more electronegative element over oxygen, entered the compound and neglected the role of oxygen in thermal oxidation, instead reducing sulfur content of pyrite to only form pyrrhotite.

Keywords: roasting; pyrite; iron oxides; pyrrhotite; hydrofluoric acid

1. Introduction

Metal mining operations generate a considerable amount of waste rock and mine tailings. The latter is finely grounded during the mineral processing and is highly reactive due to the small size. Mine tailings may contain base transition metals such as iron (Fe), precious metals like gold (Au), or toxic elements including arsenic (As), in different forms such as oxides, sulfides, and hydroxides [1,2]. Due to the presence of various impurities such as silicates and aluminosilicates and the complexity of the chemical and mineralogical compositions, mine tailings recovery and reuse are difficult [3,4]. However, due to the depletion of global ore deposits and continuous high demands for metals,



the recycling and reusing of mine tailings are still an interesting topic to work on. This is of great importance, since mine tailings are already fine-grain particles that may be more economically beneficial over the extraction of deep-buried ore body [5,6].

As one of the transition-metal sulfide and gangue mineral present in igneous rocks, vein deposits, and sedimentary rocks, pyrite (FeS₂) coexists with some valuable minerals and metals, such as gold, copper, zinc, and nickel [7,8]. After ore beneficiation and separation of gangue minerals from ore body, a considerable amount of pyrite can be produced and transferred to the tailings ponds disposal [2,9]. Under the oxidative condition in the presence of oxygen and moisture, pyrite oxidizes and generates acid mine drainage (AMD), known as a critical environmental problem [10,11]. In this case, AMD treatments that increase the overall costs of the tailings' management should be applied to protect the environment [12,13]. It might be environmentally and economically beneficial if the pyrite in mine tailings could be eliminated or recovered to be usable on its original or modified form [14].

Reduction-roasting is routinely used to recover valuable minerals or remove toxic elements from a variety of combinations [15–17]. Since minerals in mine tailings are not at equilibrium state, it is believed that during the reduction-roasting, a combination of different minerals (e.g., oxides, sulfides) and released gas (carbon dioxide, sulfur dioxide) can be produced or released. For example, calcite decomposes over 800 °C and releases CO₂ whereas silicate-based minerals do not thermally decompose at the temperatures below 1000 °C [18,19]. Besides, as the temperature increases during the roasting process, particles become more prone to sintering that necessitates the performance of extra separation techniques, such as grinding, to improve the mineralogical uniformity [20,21]. Therefore, the purification of mine tailings before roasting can improve the overall mineralogical phase transformation. Reduction-roasting may also change the crystalline phase of minerals to amorphous similar to blast furnace slag as a by-product of metal recovery [22,23].

In the presence of oxygen, roasting of pyrite releases sulfur dioxide (desulfurization) that can be captured and converted to sulfuric acid, but high oxygen accessibility during the roasting may form sulfur trioxide and hamper the production of sulfuric acid [24,25]. By the occurrence of various exothermic-endothermic reactions during the pyrite's roasting, some intermediate products (minerals) may also form, depending on the overall oxygen availability-pressure and the temperature range (Equations (1)–(7)) [26,27]. Thermal decomposition of pyrite by direct or successive oxidation in an inert or oxygen-containing atmosphere generally occurs at the temperatures higher than 600 °C [18]. As the oxygen accessibility increases during the pyrite's thermal decomposition (Equation (3)), hematite (Fe_2O_3) as the main oxidation product and the most stable iron oxide at ambient condition forms, while any restriction in oxygen availability causes pyrite to mainly transform to magnetite (Fe_3O_4) (Equation (4)) [20,26,28,29]. However, in non-oxidative conditions, the thermal transformation of pyrite follows the sequence of pyrite/pyrrhotite/troilite/iron [30,31]. As the consequence of pyrite's oxidation-reduction, the magnetic properties of the formed minerals will be boosted that influences the magnetic separation efficiency [29]. The mechanism of pyrite endothermic thermal transformation to pyrrhotite, as a non-stoichiometric and transition chalcogenide iron sulfide with lower sulfur content (Equation (6)), follows the unreacted core model and is followed by zero-order surface reaction, or gas film/product layer diffusion, or a combination of these mechanisms [30]. Due to the Fe vacancy on octahedral sites, potential plateaus, and high specific capacities, pyrrhotite provides an astonishing electrochemical specification that can be used as the cathode material in lithium-ion batteries [32–34]. Pyrite to pyrrhotite mineralogical transformation requires higher temperature over the transformation of pyrite to iron oxides, while the presence of carbon dioxide may improve the overall transformation process, as shown in Equation (7) [35,36].

$$FeS_{2(s)} \rightarrow FeS_{(s)} + S_{(s)} \tag{1}$$

$$FeS_{(s)} + 5/3 O_{2(g)} \rightarrow 1/3 Fe_3O_{4(s)} + SO_{2(g)}$$
 (2)

$$1/3 \operatorname{Fe_3O}_{4(s)} + 1/12 \operatorname{O}_{2(g)} \to \frac{1}{2} \operatorname{Fe_2O}_{3(s)}$$
 (3)

$$S + O_{2(g)} \rightarrow SO_{2(g)}$$
 (4)

$$SO_{2(g)} + \frac{1}{2} O_{2(g)} \to SO_{3(g)}$$
 (5)

$$\text{FeS}_{2(s)} \to \text{FeS}_{x(s)} + (1 - 0.5_x) S_{2(s)}$$
 (6)

$$FeS_{2(s)} + 2CO_{2(g)} \rightarrow Fe_{1-x}S_{(s)} + 2CO_{(g)} + SO_{2(g)}$$
 (7)

Acid leaching of waste materials such as mine tailings is routinely performed for different purposes, such as minerals' dissolution and recovery [37–39]. However, efficient acid dissolution of target minerals could be hindered by the presence of various coexisting minerals and the formation of secondary oxidation/dissolution products [40]. To increase the concentration of pyrite in mine tailings, acid leaching is not proposed, since most of the acids dissolve pyrite [41,42]. Hydrofluoric acid (HF) that leaches most inorganic minerals including aluminosilicates through etching effect has no influence on pyrite and can be used to boost the pyrite content of mine tailings [43–45]. Equation (8) presents the theoretical reaction of silica with hydrofluoric acid, while silicon tetrafluoride and water are the main output of the reaction. During the leaching process, silicon tetrafluoride may react with the present metal and metalloid ions in mine tailings to precipitate as some new compounds [46,47]. Further roasting of enriched pyrite tailings generates a more homogeneous combination, while decreasing the sintering possibility simultaneously.

$$4HF_{(aq)} + SiO_{2(s)} \rightarrow SiF_{4(g)} + 2H_2O_{(l)}$$

$$\tag{8}$$

The originality of the present study was to partially valorize sulfidic mine tailings by the thermal transformation of pyrite under the oxidative roasting process to a more valuable mineral that can be magnetically recovered. The novelty of this study was to beneficiate the pyrite content of mine tailings using hydrofluoric acid leaching, to improve the quality and quantity of the thermally transformed form of minerals. The influence of hydrofluoric acid pretreatment combined with the roasting operation was also investigated on the mineralogical phase transformation of pyrite.

2. Materials and Methods

2.1. Materials Collection and Preparation

Sulfidic tailings used in this study were sampled from a polymetallic underground hard rock zinc mine located in Turkey (41.040231° N, 40.765379° E). The provided tailings were first dried and then underwent physical, chemical, and mineralogical assessments. Table 1 presents the mineralogical and elemental compositions of the as-received tailings estimated by X-ray diffraction (XRD, Xpert MPD, cobalt tube, voltage 40 kV, current 40 mA, X'Pert software) and inductively coupled plasma optical emission spectrometry (ICP-OES, Model 730-ES, Varian Company, Palo Alto, CA, USA). Table 2 presents the physical characterizations of the tailings including relative density, specific surface area (characterized by BET test), and cumulative particle size distribution (determined by Malvern[®] Mastersizer S2000). Hydrofluoric acid (HF 40%, Merck-100335) was also used to enrich the pyrite content of the tailings by leaching.

Table 1. Main chemical and mineralogical composition of the tailings.

Elemental	Composition	Mineralogy
Element	wt%	
Al	2.742	Quartz (SiO ₂)
As	0.008	Pyrite (FeS ₂)
Si	20.9	Smithsonite ($ZnCO_3$)
Ca	1.242	Diopside (CaMgSi ₂ O ₆)
Cu	0.264	Calcite (CaCO ₃)

Elemental	Composition	Mineralogy					
Element	wt%						
Fe	17.3	Albite (Na, Ca)Al(Si, Al) ₃ O ₈					
Κ	0.428	Sodium copper sulfide $Na(Cu_4S_4)$					
Na	0.174						
Mg	1.271						
Zn	0.342						
S	15.09						

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Specific Surface Area	Relative Density	Particle Size Distribution					
(m ² /g)	(g/cm ³)	(μm)					
3.51	3.72	d(10%): 8.6	d(50%): 73.67	d(80%): 134.89	d(90%): 176.67		

2.2. Tailings Leaching and Roasting

To boost the pyrite content, 30 g of mine tailings were left in 90 mL cold hydrofluoric acid (40%) for 24 h. After this period, a highly agglomerated white to gray minerals (slag tailings) accumulated on top of the leached tailings; both components underwent continuous washing followed by drying before further analyses. The roasting process was performed using a laboratory high-temperature muffle furnace. Based on trial and error at lab scale, when the temperature value was changed between 700–1000 °C for a particular time between 5–60 min, roasting at 1000 °C for 15 min was found to be the optimum temperature and time that removed the maximum elemental S from the specimen, possibly in the form of SO₂ or based on Equations (1) and (6) during pyrite thermal decomposition. In each cycle of the roasting experiment, the oven's temperature fixed at 1000 °C, and 30 g of tailings were placed in the porcelain crucible and left in the lab atmosphere for stabilization and oxidation accomplishment.

2.3. Complementary Analyses and Tests

Different methods were used to characterize the influence of roasting and acid dissolution (leaching) on the mineralogy and chemical configuration of tailings. X-ray diffraction (XRD, Xpert MPD, copper tube, voltage 40 kV, current 40 mA) combined with Rietveld refinement method was performed to identify the mineral phases and quantification using materials analysis software (MAUD) [48]. Fourier transform infrared spectroscopy (FTIR, Bruker Optics Tensor 27 Spectrometer, 200 independent scans, resolution of 2 cm⁻¹, 4000–400 cm⁻¹) and thermogravimetric analysis (TG, NETZSCH STA 449 JUPITER, nitrogen gas, 10 °C/min to 1000 °C) were utilized to identify the chemical and mineralogical changes as well. Scanning electron microscopy and energy dispersive spectroscopy detector (SEM-EDS, JEOL JSM 6010 LV, OXFORD XMAX 20, 5 kv electron emission and 20 kV emission voltage) were also performed to observe the microstructure and elemental compositions of the samples. Nitrogen adsorption-desorption isotherm was also used to determine the influence of acid dissolution and roasting on surface properties of the specimens including Brunauer-Emmet-Teller (SBET) surface area, total pore volume ($p/p_0 = 0.990$), and mean pore diameter at 77 K using BELSORP MINI II. Before BET analysis, samples were purged with nitrogen gas for 2 h at 120 °C using BEL PREP VAC II. For magnetic properties evaluation, vibrating sample magnetometer (VSM), the magnetic measurement has been carried out at room temperature with an applied field of 10 kOe. A magnetic stirrer with 1000 rpm spinning speed was used to separate the magnetic particles. In this case, water was firstly poured into the beaker (250 mL) containing a 40 mm Teflon covered stirrer bar, then tailings were added to the solution (solid/liquid ratio: 1:200) and stirred for 10 min at lab atmosphere. At the end of the experiment, the stir bar containing adhered magnet particles removed from the beaker and underwent drying and mass measurement. Based on the mass of stir bar, dried adhered particles, and the initial mass of the tailings, the recovery rate (wt%) was calculated. This inaccurate method was used due to the lack of proper equipment and insufficient amount of materials and it is not generally recommended.

3. Results

3.1. XRD Experiment

Figure 1 presents the XRD results of acid leaching on mineralogical changes of the tailings. As can be seen, a considerable amount of quartz (SiO₂) was dissolved by hydrofluoric acid as the intensity of the pertinent peaks reduced in leached tailings. In addition, carbonates including smithsonite (ZnCO₃), calcite (CaCO₃), and dolomite (CaMg(CO₃)₂) were also dissolved by HF, as the related peaks were disappeared in leached tailings. However, HF did not leach pyrite (FeS₂), as the relevant peaks remained constant in the leached tailings. As shown in Figure 1, the newly formed minerals in slag tailings are mainly aluminum hydroxide (Al(OH)₃ or gibbsite) and fluorine-dominate minerals, including Frankamenite (K₃Na₃Ca₅(Si₁₂O₃₀)F₂(OH)₂·(H2O)), calcium silicon fluoride hydrate (CaSiF₆·2H₂O), and potassium aluminum fluoride hydrate (KAIF₄.H₂O). A minor amount of iron oxide (magnetite or Mn₃O₄), iron sulfate (rozenite or Fe₂SO₄·4H₂O), and polymorph silica (cristobalite) were also formed, while the precipitated slag tailings could be physically removed from the leached tailings. The leaching condition of this study was suitable to form a considerable amount of gibbsite as the reaction between Al³⁺ and OH⁻ ions (2 θ ~18 in slag tailings), indicating higher reactivity of aluminium ions (Al) with OH over fluorine (F). The evolved peak at $2\theta = 17$ in slag tailings remained unknown. Equation (9) proposes the chemical reaction between hydrofluoric acid and existing minerals in the tailings.

$$\begin{split} & FeS_{2(s)} + SO_2 + ZnCO_{3(s)} + CaMgSi_2O_{6(s)} + 4 CaCO_{3(s)} + (Na, Ca) Al (Si, \\ & Al)_3O_{8(s)} + MgCO_3.3H_2O_{(s)} + 2NaCuS_{(s)} + BaMg_2(Al_6Si_9O_{30})_{(s)} + 14HF_{(aq)} \\ & + 10H_2O_{(l)} \rightarrow SiO_{2(s)} + FeS_{2(s)} + Zn^{+2}{}_{(aq)} + Mg^{+2}{}_{(aq)} + 2CaSiF_6.2H_2O_{(s)} + \\ & K_3Na_3Ca_4Si_{12}O_{30}F_2.(OH)_2.H2O_{(s)} + Cu^{+2}{}_{(aq)} + 10Al(OH)_{3(s)} + Ba^{+2}{}_{(aq)} + 2CO_{2(g)} \\ & + SO_4^{-2}{}_{(aq)} + O_{2(g)} \end{split}$$
(9)



Figure 1. XRD results of hydrofluoric acid leaching on tailings.

Figure 2 displays the influence of roasting (15 min at 1000 °C) on acid leached and raw (original) tailings. As can be seen, the roasting of raw tailings mainly transformed pyrite to iron oxides including magnetite and hematite (Fe₂O₃), whereas in acid leached tailings, pyrrhotite (Fe_{0.95}S) was the major formed mineral.



Figure 2. XRD results of roasted tailings specimens.

Table 3 provides the influence of roasting and acid leaching on crystallinity, amorphousness, and quantities of SiO_2 and iron minerals extracted from Rietveld analysis [49]. Since raw tailings were produced from different chemical and physical operations during mineral processing, only 27% of the overall minerals were crystalline. In addition, 28.4 wt% of the minerals in raw tailings were composed of smithsonite, diopside, calcite, albite, and sodium copper sulfide, while pyrite and silica are the main mineralogical compositions (71.6 wt%). Roasting and acid leaching procedures also reduced the crystallinity and increased the amorphousness phases of minerals. Based on Table 3, the acid leaching increased the overall pyrite content, while roasting completely transformed pyrite to pyrrhotite.

	Minerals%								
Specimen	Silicon Dioxide (wt%)	Pyrite (wt%)	Pyrrhotite (wt%)	Hematite (wt%)	Magnetite (wt%)	Crystallinity (%)	Amorphous Phases (%)		
Raw tailings	39.2	32.4	-	-	-	27	73		
Roasted raw tailings	14.8	0.7	-	41.5	1.7	15.6	84.4		
Leached tailings	25.9	74.1	-	-	-	19.2	80.8		
Roasted leached tailings	20.8	-	79.2	-	-	12.6	87.4		
Slag tailings	3.1	11.2	-	-	7.2	33	67		

Table 3. The obtained results from Rietveld analysis.

3.2. Thermogravimetric Analysis

Figure 3a,b display the differential thermogravimetric (DTG) and thermogravimetric (TG) graphs of raw, acid leached, and slag tailings. The emerged peak between 620 to 670 °C presents the thermal decomposition of pyrite. This peak in acid leached and raw tailings are approximately similar (Figure 3a) equal to approximately 14.5% mass loss (Figure 3b). There are two minor peaks in slag tailings at approximately 620 and 570 °C (Figure 3a), indicating the presence of pyrite with 3.5% and rozenite with 1.5% mass loss [18]. The major peak at approximately 330 °C in slag tailings (Figure 3a) with 64.5% mass loss (Figure 3b) presents the formation of gibbsite as the main mineral, which is a well-known compound in bauxite [50,51].



Figure 3. Differential thermogravimetric (**a**) and thermogravimetric (**b**) graphs of raw, acid leached, and slag tailings.

As Figure 4a,b illustrate the DTG and TG thermographs of roasted raw and roasted acid leached tailings, no thermal decomposition peak for pyrite available anymore. The identical weight loss (1.55 wt%) at approximately 520 °C represents the minor formation siderite (FeCO₃) indicating the marginal reactivity of carbon dioxide with iron ions [52,53]. Figure 4a also displays a negligible reactivity of calcium ions with carbon dioxide in roasted raw tailings at approximately 800 °C by the formation of CaCO₃ [10].



Figure 4. Differential thermogravimetric (a) and thermogravimetric (b) graphs of roasted tailings.

Figure 5 displays the influence of acid leaching and roasting on the chemical condition of minerals through infrared spectroscopy. The emerged peaks at 3544-3332 and 1630-1740 cm⁻¹ are attributed to –OH groups of hydrated minerals such as iron sulfates; the frequency bands between 2800 and 3000 cm⁻¹ are assigned to the stretching vibration of CO₂, and the bands at 1380 and 1450 cm⁻¹ implicate the presence of carbonates [10,54]. The derived peaks at approximately 568, 791, and 1082 cm⁻¹ were attributed to symmetric stretching of Al–O–Si and Si–O–Si bands [55]. The emerged peak at 1082 cm⁻¹ could also present the S–O adsorption band of SO₄^{2–} pertinent to thermal oxidation of pyrite [56]. The emerged peak at 730 cm⁻¹ in slag tailings, which is similar to the 791 cm⁻¹ peak in other specimens, indicates the structural changes of silicon-based minerals [57]. The emerged stretching band at approximately 430 cm⁻¹ in raw and leached tailings (Figure 5a) is attributed to pyrite [58,59]. This peak in roasted specimens moved and overlapped with the stretching band at 460 cm⁻¹ that may demonstrate the transformation of pyrite to pyrrhotite (Figure 5b). The stretching band at approximately 687 cm⁻¹ in roasted raw and slag tailings ascribed to iron oxides as the other thermally transformed form of pyrite [60,61]. The two stretching bands in slag tailings at 730 and 1423 cm⁻¹ illustrate the formation of fluoride-based minerals [62,63].



Figure 5. FTIR spectrum of (a) raw-leached-slag tailings (b) roasted raw-leached tailings.

3.4. Microstructural and Elemental Characterization

Figure 6 displays SEM micrographs (50-100 μ m) and related EDS elemental mapping, while the average extracted elemental concentrations are included in Table 4. Based on Figure 6a,b and Table 4, a considerable amount of elemental sulfur was reduced due to the roasting process. It is also evident that the oxygen and iron elements in roasted raw tailings (Figure 6b) are well linked, indicating the formation of iron oxides. In acid leached specimen (Figure 6c), the concentration of iron and sulfur are higher over the rest of the elements (Table 4), implicating the ineffectiveness of hydrofluoric acid leaching on pyrite. The concentration of silicon (Si), aluminum (Al), fluorine (F), and oxygen elements in acid leached specimen presents the newly formed minerals and leftover silicate or aluminosilicate minerals from tailings, which is in good agreement with XRD results. A more extensive hydrofluoric acid leaching may be necessary to dissolve silicate-based minerals to a higher level. The interrelation between iron and sulfur elements in roasted leached specimen (Figure 6d) displays the formation of pyrrhotite as the thermal transformation of pyrite. In contrast to the roasted raw tailings specimen (Figure 6b), no iron oxide was formed, due to the thermal oxidation of pyrite in the acid leached sample. A high concentration of fluorine, silicon, and aluminum ions in slag tailings (Figure 6e) can be seen, that declares the effectiveness of HF to dissolve minerals containing such ions. Additionally, there is a minor amount of iron connected with sulfur and oxygen (Figure 6e), indicating the physical displacement of pyrite and marginal formation of iron sulfate (rozenite), and iron oxides (magnetite).



Figure 6. SEM images (50–100 μ m) and EDS mapping of (**a**) raw, (**b**) roasted raw, (**c**) leached, (**d**) roasted leached, (**e**) slag tailings.

Table 4. The semi-quantitative average elemental compositions extracted from EDS Map spectrum.

Specimen -				El	ements (v	vt%)			
	Al	Si	Ca	Mg	Fe	S	0	К	F
Raw tailings	3.5	16.4	0.8	1	22.9	14.9	28.6	0.6	-
Roasted raw tailings	4.7	15.1	2.8	1.5	37.6	4.6	24.7	0.7	-
Leached tailings	2.7	10.6	0.8	1	24.5	21.6	13.6	0.2	13.6
Roasted leached tailings	9.7	10.2	0.8	4.5	27.8	8.7	15.5	0.2	14.7
Slag tailings	3	12.8	1.9	1.1	13.1	5.9	0.7	0.7	48.2

The surface characteristics of raw, leached, and roasted tailings specimens are summarized in Table 5. It is evident that the roasting process increased the surface area, total pore volume, and mean pore diameter of the tailings up to 4%, 13%, and 8%. Acid leaching made this difference to a higher level, including 27%, 101%, and 58% increases in surface area, total pore volume, and mean pore diameter. Roasting of leached tailings similarly increased less than 1% surface area, 14% total pore volume, and 1.5% mean pore diameter over the leached tailings. It is evident that both acid leaching and roasting procedures made the overall minerals more porous, due to the dissolution influence or impurities removal from the pores of minerals.

Sample	S_{BET} (m ² ·g ⁻¹)	Total Pore Volume (cm ⁻³ ·g ⁻¹)	Mean Pore Diameter (nm)
Raw tailings	3.675	0.0183	20.01
Roasted raw tailings	3.858	0.0209	21.70
Leached tailings	4.688	0.0370	31.62
Roasted leached tailings	4.731	0.0423	32.11

Table 5. Structural surface characteristics of the specimens.

3.6. Magnetic Properties Results

Figure 7 displays the M-H curve of the magnetically separated roasted specimens. As can be seen, the magnetization saturation (MS) occurred at a low external field (~2000–3000 Oe), while the achieved MS values for magnetically roasted raw and magnetically roasted leached tailings were 37.16 and 31.8 emu/g. A higher MS value indicates the emergence of divalent metal ions such as Fe²⁺ [64]. The MS values of pyrite, pyrrhotite, hematite, magnetite, siderite, and calcite are 0.3, 2800, 20.6, 15,600, 331.45, and 0.75 emu/g [65]. Based on Figure 7, roasted raw tailings displays a higher magnetic property over the roasted leached tailings, since they mainly consist of iron oxides. The results of wet magnetic separation also confirmed that 54% of the roasted raw tailings were recovered over the 32% magnetic recovery of the roasted leached specimen. Table 6 displays the elemental EDS mapping analysis of magnetically separated specimens.



Figure 7. Magnetic hysteresis curves of roasted raw and roasted acid leached tailings.

Specimen				El	ements	(wt%)			
	Al	Si	Ca	Mg	Fe	S	0	К	F
Magnetically separated roasted raw tailings	5.3	11.8	2.9	1.6	53.8	6	13.4	0.8	-
Magnetically separated roasted leached tailings	0.3	7.54	-	-	47.5	28.5	8.5	-	2.6

Table 6. The semi-quantitative average elemental compositions of magnetic separated specimens fromEDS Mapping.

4. Discussion

4.1. Thermal Oxidation

As the results of this study indicated, hydrofluoric acid leaching was considerably beneficiated by the pyrite content of sulfidic mine tailings. However, when the beneficiated mine tailings underwent the roasting process, the pyrite completely transformed to pyrrhotite, another iron sulfide with lower sulfur content. Pyrrhotite formation from pyrite mainly occurs in the absence of oxygen [30], but in this study, oxygen was available to all the roasted specimens. To scrutinize the achieved results, the residue of raw tailings after thermogravimetric test underwent XRD analysis and it was found that all the pyrite minerals transformed to pyrrhotite, which is perceivable, due to the absence of oxygen. Therefore, leftover fluorine ions or newly formed fluorine-based minerals in leached tailings neglected the role of oxygen in the thermal transformation of pyrite to iron oxides. Fluorine is a more electronegative element than oxygen, but at the level of this study, with the current tests and methods, it was not possible to elucidate the exact mechanism of fluorine that declined the role of oxygen in the thermal transformation of pyrite. This is quite a new and considerable achievement, because if fluorine could also diminish the role of oxygen in the oxidation of pyrite in wet chemistry, one of the most challenging environmental concerns originated from mining activities, acid mine drainage (AMD), may be controllable. In this case, use of less hazardous fluorine-based components such as sodium fluoride should be examined, to see if there is any competition between the fluorine and oxygen ions, which occurs during the wet chemical oxidation. As Equation (8) proposes, a considerable amount of HF transfers to H_2O and SiF_4 , but the leftover acid residue may still be useable in a new leaching process depending on the quality of the acid; acid neutralization with lime can also be considered to protect the environment.

4.2. Sintering and Technological Aspects

Both roasted raw and roasted leached tailings were magnetically recovered (54 and 32 wt%), but the recovery rate in the oxide-based combination was higher than that of sulfide-based [66]. This is noticeable, since the magnetic saturation value of pyrrhotite is higher than that of hematite [65], but apparently the roasting process was more efficient in improving the magnetic properties of iron oxides. The recovered minerals still contain some impurities (e.g., silicates), implicating the sintering influence of the roasting process. Figure 8 displays the sintered silica particles on the surface of iron oxide particle on magnetically separated roasted raw tailings. To improve the magnetic separation quality, performing secondary operation such as milling is necessary. A dedicated section in the mineral processing plant at mine site should be established for the proposed mine tailings valorization. This section should consist of a roasting part (e.g., furnace) and pools or containers for acid leaching (for pyrrhotite generation). The reusing or neutralization of acid after leaching should be estimated on-site depending on the quality of leftover acid. However, some of the instruments, such as grinders and separators are available in the mineral processing plant that may legitimate the tailings thermal treatment on mine site, collection, and transportation of mine tailings to a metallurgy plant (iron and steel industry) is another option that should be considered and evaluated based on capital.



Figure 8. EDS images of magnetically separated roasted raw tailings.

5. Conclusions

Acid leaching and roasting procedures are used to valorize and purify sulfidic mine tailings in this study. It was found that the oxidative roasting process of the sulfidic mine tailings containing 32.4 wt% pyrite at 1000 °C for 15 min boosted the iron oxide content (hematite) of the combination by up to 41.5%. At the same condition when hydrofluoric acid beneficiation was applied to remove silicate-based minerals from mine tailings, the pyrrhotite content of the compound elevated to 79.2 wt%. Based on SEM-EDS observations, the presence of elemental fluorine ions or formed fluorine-based minerals during acid leaching prevented the thermal transformation of pyrite to iron oxides, indicating a competition between fluorine and oxygen ions during thermal oxidation. The roasting process improved the overall magnetic properties of hematite more importantly than that of pyrrhotite, even though the original magnetic saturation value of pyrrhotite was higher. In this case, the magnetic recovery rate of the hematite-based compounds was 54 wt%, while the magnetic recovery rate of pyrrhotite-based mixture was 32 wt%. Silica particles could not be completely separated from iron oxides due to the sintering influence that necessitates the performance of secondary operations such as milling.

Author Contributions: Conceptualization, B.K. and A.K.D.; Methodology, B.K., P.M. and E.D.; Data Curation, B.K. and E.Y. (Erol Yilmaz); Formal Analysis, A.K.D. and E.Y. (Erol Yilmaz); Investigation, B.K., P.M. and E.D.; Writing—Original Draft Preparation, B.K. and A.K.D.; Validation, Writing—Review and Editing, A.K.D., E.Y. (Erol Yilmaz), P.M., E.D. and E.Y. (Elif Yilmaz); Visualization, all; All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by Iran National Science Foundation (INSF) with a research grant (NO:96016805, 2018).

Conflicts of Interest: The authors declare no conflict of interest.

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