ABSTRACT: Al Amar gold ore is rich in sulfides of base metals and is commercially applied for the production of copper concentrate via flotation and gold bullion by cyanidation of tailing. The current process flowsheet suffers from low gold recovery (~60%) and loss of metals in the hazardous stockpiled residue. This work addresses these drawbacks by a newly experimental redesign of the process circuit. The innovative flowsheet comprises a sequence of operations, including acid leaching of the roasted ore, gold recovery from the leach residue, and preparation of a valuable zinc−copper−lead ferrite from the filtrate by coprecipitation followed by heat treatment. The ore is roasted at 650 °C and then leached in 20% HCl, where most of Zn, Cu, Pb, and Fe contents are dissolved, while pristine gold remains in the residue. Most of the gold (~93%) can be recovered by cyanidation of the acid leach residue. Stoichiometric ratios of dissolved Zn, Cu, Pb, and Fe in the acid leach solution can be kept at 0.6:0.3:0.1:2.0, respectively, only by adding a small amount of ferric chloride. These metals are coprecipitated at varying pH values from 8 to 10, and the produced powders are annealed at temperatures from 600 to 1100 °C. X-ray diffraction (XRD) charts reveal sharp peaks of the targeted $\text{Zn}_0.6\text{Cu}_{0.3}\text{Pb}_{0.1}\text{Fe}_2\text{O}_4$ phase at 600 °C, while a highly crystalline single phase is obtained at 1100 °C, independently of precipitation pH. The finest size is found at pH 12. Scanning electron microscopy (SEM) investigation shows uniform cubic microstructures of samples annealed at 1100 °C. The produced ferrite powders exhibit soft magnetic characteristics. Saturation magnetization, $M_s$, substantially increases with pH. Coercivity, $H_c$, increases with increasing annealing temperatures, from 600 to 800 °C, and decreases above 800 °C. Preliminary cost−benefit analysis revealed that the profit margin of the proposed process flowsheet is promising. The wastewater is almost free of heavy metals. Our advances in high gold recovery and preparation of valuable magnetic nanocrystalline ferrite provide exciting opportunities to enhance and maximize Al Amar ore production for practical applications.

I. INTRODUCTION

A polymetallic gold ore in the Al Amar region, Saudi Arabia, is rich in sulfide minerals of base metals, namely, sphalerite ($\text{ZnFeS}_2$), pyrite ($\text{FeS}_2$), chalcopyrite ($\text{CuFeS}_2$), and a minority of galena ($\text{PbS}$). The ore is commercially exploited since 2006 at a production rate of 200 000 t/year. Figure 1a shows a simplified sequence of industrial operations currently applied on-site at the Al Amar gold mine. A saleable copper concentrate is separated from the ground run-of-mine (ROM) by floatation, and gold in the floatation tailing is recovered by the carbon-in-leach (CIL) cyanidation process. This flowsheet suffers from the low recovery of gold and massive loss of metals rejected in the final residue. Moreover,
residues stockpiled near the mine site are considered as hazardous materials due to high contents of heavy metals. Only ∼60% of gold in the CIL feed of Al Amar ore can be recovered by cyanidation, whereas the remaining ∼40% is found in the residue. The extraction of gold is mostly affected by the mineralogical nature of the ore. Fine dissemination of gold particles encapsulated within the hard sulphide matrix was found to be the main reason for the poor yield of gold in the Al Amar ore.1−3 Unlocked gold particles are extracted while the trapped ones are inaccessible and remain in discarded wastes. Due to the continuous depletion of ores, it becomes more imperative to maximize the efficiency of gold recovery of the mined ones.

Approximately three quarters of Al Amar ROM ore (150 000 t/year) is dumped into the residue with high contents of zinc, iron, lead and low content of gold, causing environmental hazards and significant loss of capital. It is estimated that ∼260 000 t of Zn, ∼126 000 t of Fe, ∼2200 t of Cu, ∼800 t of Pb, and ∼2.3 t of Au are accumulated in the residue. This residue can be considered as a secondary source since it holds substantial quantities of valuable metals. We have found that the lost gold cannot be completely recovered (∼50%) from this residue, even after applying severe roasting and leaching conditions.2 In agreement with these results, Liu et al. stated that gold recovery from roasted sulfidic-ores remained well below the acceptable levels.5 Although roasting is a common practice for the pretreatment of sulfidic gold ores, it may be insufficient to achieve a satisfactory gold recovery.5,6 This may be due to partial liberation of gold and insufficient contact with the leaching medium.

Free-milling gold ores are usually reactive toward leaching with cyanide and characterized by high recovery (<90%).7 Refractory ores are those yielding low gold recoveries (>80%) even with extremely high consumption of reagents.8 The mineral structure and the nature of gold association play an important role in the refractoriness. To date, several alternatives have been explored and practiced to overcome the poor recovery of gold from refractory ores, including appropriate pretreatment methods of ultrafine grinding, pressure or biological oxidation, and alkaline leaching in addition to roasting.9−13 These technologies have several advantages in overcoming the refractoriness through releasing the disseminated fine gold and improving the action of leaching reagents. However, they suffer from some technical constraints such as high energy consumption, process complications, and low recovery.
Acidic preleaching of gold ores was examined to remove the copper contents of oxidic nature, which are causing high cyanide consumption and low gold recovery. Gold recovery has been noticeably intensified through acidic and alkaline separate pretreatment of coarse and fine size fractions of refractory concentrate calcine. Diverse options of operations should be redesigned to control the economics of this particular process.

In this work, a novel sequence of operations is developed to ensure maximum recovery of gold and valuable metals from the Al Amar ore. The proposed flowsheet addresses the inherent limitations of current processes while satisfying the market’s needs for large-scale production of advanced magnetic materials for modern applications. The sequence of operations, shown in Figure 1b, comprises acid leaching of the roasted ore, recovery of gold from the leaching residue, and preparation of magnetic ferrite from the filtrate by coprecipitation, followed by heat treatment. The acid leachate is enriched with iron added as ferric chloride to raise the iron content to the level that is suitable for targeted ferrite preparation. After coprecipitation, the depleted leach liquor can be treated for the recovery of the left trace metal contents before rejection as a waste stream. Figure 2 shows a schematic representation of the proposed mechanism during roasting, acid leaching, and cyanidation of a gold-disseminated metal sulfide ore. Roasting of ground ROM in an oxidizing atmosphere breaks up hard mineral crystals and converts metal sulfides into the corresponding oxides. The latter can be simply leached in a suitable acidic medium to dissolve base metals, while gold is retained unattacked. Most gold particles in the depleted residue will be accessible to the lixiviant action during cyanidation. This is expected to improve the gold recovery remarkably. An advanced ferrite can then be produced from the dissolved metals in the filtrate under controlled conditions of coprecipitation and subsequent heat treatment. This procedure enables profitable exploitation of base and precious metals in Al Amar ore, which are currently wasted due to the drawbacks of the existing sequence of operations.

Nanostructured ferrite materials retain exceptional electrical and magnetic characteristics and are widely studied and applied for biomedical, catalysis, optical, electronic, and other vital applications. Spinel ferrites that have formula \(\text{MFe}_2\text{O}_4\) (M: Mn, Co, Ni, Cu or Zn or a mixture of them) possess excellent chemical stability and physical and electronic structures. These materials have been technologically integrated into electronic devices, high-density information storage, gas sensors, magnetic resonance imaging, medical diagnostics, drug delivery, catalysts, and high microwave applications. Recently, their antibacterial activity, photo-degradation, and removal of heavy metals were also evaluated. Spinel ferrites accommodate cations among two possible available interplanar sublattices, tetrahedral (A) sites, and octahedral (B) sites. Spinel structure ferrites can be either normal spinel (\(\text{M}^{2+}\)\(_6\)(\(\text{Fe}^{3+}\)\(_{12}\)\(\text{Fe}^{3+}\)\(_{16}\))\(_6\)) or inverse spinel with half of the trivalent ions in the A sites and the other half together with divalent ions in the B sites. Thus, the magnetic and physical properties of these ferrites are determined by the substitutions of various kinds of \(\text{M}^{2+}\) among divalent cations (e.g., \(\text{Zn}^{2+}\), \(\text{Mn}^{2+}\), \(\text{Ni}^{2+}\), \(\text{Mg}^{2+}\), \(\text{Co}^{2+}\), \(\text{Cu}^{2+}\)) as well as the preparation conditions.

Depending on the annealing history and the preparation route, zinc–copper ferrite (\(\text{Zn}_1-x\text{Cu}_x\text{Fe}_2\text{O}_4\)) shows a considerable variation in its atomic arrangement, which may be attributable to the distribution of Zn, Cu, and Fe cations between the two nonequivalent lattices, tetrahedrally coordinated sites (A), and octahedrally coordinated sites (B). It has been pointed out that the distribution and the valance of metal cations on these sites determine the magnetic and electrical properties.

Spinel-structured copper and zinc nanocrystalline ferrites have been synthesized by several chemical methods such as coprecipitation, precursor coprecipitation, sol–gel auto-combustion, electrospinning combined with sol–gel, the standard ceramic method, and the hydrothermal method. Among these techniques, coprecipitation enhances the degree of homogeneity and contact between the metallic components and ensures excellent properties of the final product. Although these processes produce high-quality spinel ferrites, they require complicated procedures, and most of the starting materials are expensive pure chemicals. These constraints severely limit the commercial scalability of these processes and make the price of the produced ferrite expensive. On the other hand, massive quantities of inexpensive raw materials such as natural ores or waste products rich in base metals are found in many countries. However, studies on their application for the synthesis of nanocrystalline ferrite products are rare.

Sludge precipitation of heavy metals has been attempted during the treatment of acid mine drainage (AMD) through neutralization at pH 8.5. The study was limited to precipitation with no subsequent heat treatment, and thus yielded a material of very low magnetic properties. Bismuth and calcium nanoparticle ferrites were synthesized using natural hematite by the sol–gel annealing technique. Doping with lead enhanced the magnetic properties of the prepared ferrites. However, expensive metallic compounds other than iron were utilized. These limitations stimulated our interest to find out an appropriate inexpensive source of raw materials to be suitable for large-scale production of nanocrystalline ferrite.

The objective of this work is to devise a novel, redesigned flowsheet of Al Amar ore to be adapted for the production of a valuable magnetic ferrite and simultaneous improvement of gold recovery. The developed design will eliminate dumping huge wastes containing gold and base metals and utilize this cheap metal source for the production of valuable advanced materials instead of expensive pure chemicals. The novelty of this work lies in developing and application of a new design of process circuit flowsheet of a gold ore to be directed toward double goals: improving gold recovery and production of a magnetic nanocrystalline ferrite from cheap starting materials instead of dumping huge wastes containing gold and base metals. Acid leaching of ROM, cyanidation of leach residue, and preparation of magnetic nanocrystalline ferrite are assessed, and the properties of the resulting materials are thoroughly investigated. The suitable conditions for maximum dissolutions of metals from roasted ROM are optimized. The mole ratios of Cu, Zn, Pb, and Fe in the acid leach liquor are adjusted to the desired target values. The copper–zinc–lead nanocrystalline ferrite is then prepared by a coprecipitation technique. The pH of the leach liquor is adjusted to alkaline values from 8 to 12, and coprecipitated metals are heat treated at different temperatures from 600 to 1100 °C. The formed phases and lattice parameters are identified by X-ray diffraction (XRD), and the morphology of microstructures are investigated by scanning electron microscopy (SEM). The magnetic properties of the formed powders are systematically investigated.
II. RESULTS AND DISCUSSION

II.I. Acid Leaching of Al Amar Ore. The chemical composition of Al Amar ROM (Table 1) indicates that it contains 6.47 ppm gold and is rich in base metals such as zinc (12.6%), iron (17.3%), copper (5.7%), and lead (5.6%). In practice, copper is separated by floatation to yield a saleable copper concentrate, gold is partially recovered from flotation tailing in the CIL circuit, and the rest of the metals are wasted in the final residue together with considerable losses of gold. These wastes are a valuable source of zinc, iron, and lead, but it is deficient in copper. Thus, the residue is a commercially worthless material for the production of copper–zinc ferrite since the copper content is very low. However, the raw ore can be considered as an attractive source for the production of the valuable copper–zinc ferrite since it contains all of the required metals in sufficient amounts. The ROM cannot be used directly for this purpose by the common ceramic method because it contains large amounts of impurities such as silica and gangue. It is apparent that if the metallic contents in the ROM can be dissolved efficiently, the produced leach solution can be considered as a suitable source for the production of the targeted ferrite. Therefore, the primary stage was to treat ROM to convert these metals into their soluble aqueous forms utilizing the hydrometallurgical techniques.

Hydrochloric and sulfuric acids are tested here as they are known as common and powerful leaching reagents forming the corresponding readily soluble chloride and sulfate ions or complexes of copper, zinc, and iron. Lead forms slightly soluble chloride, PbCl$_2$ ($K_{sp} = 1.7 \times 10^{-5}$), and lead sulfate PbSO$_4$ ($K_{sp} = 2.5 \times 10^{-8}$) salts. In chloride media, lead chloride forms soluble chloro complexes:

\[
PbCl_2(aq) + Cl^- \rightarrow [PbCl_3]^-_{(aq)} \quad (1)
\]

\[
PbCl_2(aq) + 2Cl^- \rightarrow [PbCl_4]^{2-}_{(aq)} \quad (2)
\]

A variety of negatively or positively charged lead chloro complexes with the general formula [PbCl$_x$]$_n$$^{+}$-$n$ can be found in chloride media. However, this is not the case when lead sulfate is dissolved in sulfate media. It was stated that leaching metal sulfides with hydrochloric acid is faster than leaching with sulfuric acid of the same concentration under similar conditions. Both acids are known to be commercially applied in diverse industrial processes and will be examined here for the extraction of base metals.

Acid leaching of Al Amar ROM was performed to extract the metallic contents as much as possible. Three ROM samples were investigated, namely, ground ROM as received, roasted ROM at 650 °C, and at 800 °C. XRD patterns of these samples are illustrated in Figure 3. The mineralogical compositions of the three samples were identified based on the main peaks and are listed in Table 2. The XRD chart of the ROM confirmed its sulfidic nature, where the main minerals were quartz (SiO$_2$), sphalerite-ZnFeS$_2$, pyrite-FeS$_2$, and chalcopyrite-CuFeS$_2$. The quartz was a predominant mineral. Although the chemical composition of the ROM shows the existence of lead, it does not appear in XRD charts of all tested samples. The mineralogical investigations in our previous work confirmed that the lead content in ROM of Al Amar ore is present as galena (PbS) by examinations with environmental scanning electron microscopy (ESEM). It was stated elsewhere that galena is oxidized to lead sulfate, PbSO$_4$, at 460 °C, basic lead sulfate and some lead oxide at 730–765 °C. Melting and vaporization of lead oxide were observed at 900 °C. Thus, at the applied roasting temperatures of Al Amar ore in the present work, 650 and 800 °C, the forms of lead would be as basic lead sulfate and some lead oxide.

Iron is distributed mainly in three minerals: pyrite, chalcopyrite, and sphalerite. Copper is mainly found in chalcopyrite, zinc in sphalerite, and lead in galena.

---

**Table 1. Chemical Composition of the ROM Sample of Al Amar Ore**

| element | weight percent |
|---------|----------------|
| Au      | 6.47 ppm       |
| Si      | 28.0           |
| Zn      | 12.62          |
| Fe      | 17.32          |
| Al      | 0.53           |
| Cu      | 5.73           |
| Pb      | 5.60           |
| Cd      | 0.02           |
| As      | 0.001          |
| V       | 0.56           |
| Cr      | 0.01           |
| Mn      | 0.05           |

---

**Table 2. Mineralogical Composition of the Ore and Roasted Ore at Different Temperatures**

| ROM                  | roasting at 650 °C | roasting at 800 °C |
|----------------------|--------------------|--------------------|
| quartz               | quartz             | quartz             |
| sphalerite           | hematite           | magnetite          |
| pyrite               | pyrite             | zinc oxide         |
| chalcopyrite         | copper oxide       | copper oxide       |

---

Figure 3. XRD patterns of the ROM and the ore roasted at 650 and 800 °C.
It is apparent from the XRD chart of the roasted ore, at 650 °C, that it contains oxidized forms of the corresponding sulfide minerals, including hematite (Fe₂O₃), zinc oxide (ZnO), and copper oxide (CuO) in addition to quartz, and all peaks referring to sulfide minerals (chalcopyrite, pyrite, and sphalerite) are negligible. These phase compositions of the roasted ore denote the breaking up of the crystal structure of the sulfide minerals and releasing of the metallic contents, which are oxidized by the air oxygen forming the corresponding oxides. Roasting the ore at 800 °C showed the generation of crystallographic phases of magnetite (Fe₃O₄), in addition to those of zinc oxide, copper oxide, and quartz.

The raw and roasted ROM samples were leached in mineral acids such as HCl and H₂SO₄ at boiling temperatures, and the results of metal extraction are presented in Table 3. A 20% hydrochloric acid concentration was selected as a lixiviant to ensure that it is maintained lower than its azeotropic mixture of 20.4%. Leaching of ROM in 20% HCl brought most of the zinc and lead into solution (82 and 91%, respectively), but the extraction of copper and iron was as low as 32 and 37%, respectively. This low extraction may be attributable to the known refractory nature of metal sulfides in chalcopyrite and pyrite minerals of the ore, which may need more vigorous conditions. Thus, 20% HCl is not the proper direct leaching medium because it could not decompose the iron and copper-containing minerals efficiently. The roasted ore leached in 20% HCl showed much more effective dissolution of the metals as compared with those of the raw ore. Roasting the ore at 650 °C enhanced the extraction of more than 84% of all metals in 20% HCl. Lead was the most highly extracted element (95.3%), and the extraction of other elements was in the range of 84–87%. Although lead forms slightly soluble chloride salt, PbCl₂, it can be leached out and remain soluble in chloride medium due to the formation of the corresponding chloro complexes, according to eqs 3 and 4. No improvement in extraction efficiency of all metals was detected when the roasting temperature raised to 800 °C, under similar leaching conditions.

The raw ore was leached in 20 and 80% sulfuric acid at boiling temperatures of 112 and 220 °C, respectively, and the extraction results are listed in Table 3. It can be noticed that the extraction of lead was very low (0.6%) in the studied sulfuric acid concentrations. This is mainly due to the limited solubility of lead sulfate. In 20% H₂SO₄, copper and iron were very slightly extracted (2.3 and 11.9%, respectively). A higher H₂SO₄ concentration of 80% showed much better extraction for zinc and copper (81 and 86%, respectively), but that of iron was low (33.9%). The majority of iron and lead was left in the residue after leaching in 80% H₂SO₄.

It is obvious from these results that direct acid leaching of Al Amar ROM was insufficient for the destruction of all metallic minerals and ineffective for the dissolution of the targeted metal contents. On the other hand, roasting ROM at 650 °C and subsequent leaching in 20% HCl were suitable procedures for dissolving most of all metal contents. The latter conditions were used to prepare a stock of leach solution for ferrite preparation and residue for gold recovery. It is worth mentioning that no gold was found in the leachate of all studied samples. Check tests on the residue revealed that almost all gold content remained unattacked.

It can be generally observed from results in Table 3 that the leaching rate is more favorable in HCl than in the H₂SO₄ medium. It is reported that the redox potential dependence of the chalcopyrite leaching rate in HCl solutions was very similar to that in H₂SO₄ solutions. However, the peak leaching rate was higher in HCl than in H₂SO₄. The redox potential-controlled leaching of chalcopyrite in HCl solutions is very attractive for extracting copper from low-grade copper sulfide ores.38

II. Gold Recovery. Cyanide dissolution of gold is described as follows

\[
4Au + 8NaCN + O₂ + 2H₂O \rightarrow 4Na[Au(CN)₂] + 4NaOH
\]

This follows the electrochemical equations39

\[
Au(s) + 2CN^- \rightarrow [Au(CN)₂]^- + e^- \tag{4}
\]
\[
O₂(g) + 2H₂O + 4e^- \rightarrow 4OH^- \tag{5}
\]

A stock leach residue (left after leaching roasted ore at 650 °C in 20% HCl) was used for testing the gold recovery. A series of experiments were performed to assess the efficiency of gold recovery from the acid leach residue at a varied CN⁻ concentration for 24 h. It is noticed from Figure 4 that gold recovery significantly increases with the increasing CN⁻ concentration, reaching 93% at 0.1% CN⁻, leveled off and

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c03426)

**Figure 4.** Efficiency of gold recovery from acid leach residue of Al Amar ore. S/l = 1:2, 24 h, 0.01 M NaOH.

| pretreatment and leaching conditions | leaching temperature (°C) | metals extraction (%) |
|-------------------------------------|---------------------------|-----------------------|
|                                      |                           | Zn  | Cu  | Pb  | Fe  |
| 1 20% HCl at 800 °C                 | 110                       | 82.1| 32.6| 91.6| 36.7|
| 2 20% HCl at 650 °C                | 110                       | 84.1| 86.2| 95.3| 87.1|
| 3 20% HCl at 800 °C                | 110                       | 80.2| 81.3| 91.3| 83.8|
| 4 20% H₂SO₄ at 112 °C              | 110                       | 80.6| 2.3 | 0.6 | 11.9|
| 5 80% H₂SO₄ at 220 °C              | 220                       | 81.5| 86.3| 0.6 | 33.9|

It is obvious from the XRD chart of the roasted ore, at 650 °C, that it contains oxidized forms of the corresponding sulfide minerals, including hematite (Fe₂O₃), zinc oxide (ZnO), and copper oxide (CuO) in addition to quartz, and all peaks referring to sulfide minerals (chalcopyrite, pyrite, and sphalerite) are negligible. These phase compositions of the roasted ore denote the breaking up of the crystal structure of the sulfide minerals and releasing of the metallic contents, which are oxidized by the air oxygen forming the corresponding oxides. Roasting the ore at 800 °C showed the generation of crystallographic phases of magnetite (Fe₃O₄), in addition to those of zinc oxide, copper oxide, and quartz.

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\]
remained at this high level at higher CN− concentrations. The apparent improvement in gold recovery can be attributed to the liberation of gold particles from the destructed minerals of the ore by the previous roasting and acid leaching. This will lead to a high exposure of most gold contents to the cyanide leaching medium (Figure 2). This fruitful result of the acceptable recovery of gold (93%) is considered very promising in contrast to 60% from the CIL feed of Al Amar ore. These low recoveries were attributed to the refractory nature of the mineral structures in the CIL feed, where the gold particles are finely disseminated within the hard sulfide matrix and to the incomplete liberation of gold in the roasted residue. These drawbacks are addressed in the present work by roasting and subsequent acid leaching of the ROM before cyanidation.

II.III. Ferrite Preparation and Characterization. II.III.1. Chemical Composition. Acid leaching of Al Amar roasted ROM facilitated both the dissolution of metals and recovery of gold. A stock metal solution was prepared by leaching the roasted ore (at 650 °C) in 20% HCl. This solution was used for the preparation of ferrite, and the leach residue was used for gold recovery as stated above. A precalculated amount of ferric chloride was added to a measured volume of the acid leach solution to adjust the mole ratios of Zn/Cu/Pb/Fe to the targeted one of 0.6:0.3:0.1:2, respectively.

Chemical compositions of leach liquors before and after ferrite precipitation are listed in Table 4. It can be observed that almost complete recovery of the targeted metals, Zn, Cu, Pb, and Fe, was achieved in the produced powders since traces of these metals are found in liquors after coprecipitation. Gold was not detected in all liquors, meaning that it remained almost completely unattacked in the leaching residue. Aluminum remained after precipitation in increasing amounts from liquors of pH 8−12, possibly due to its solubility as sodium aluminate at high alkaline solutions. Vanadium remained almost completely in all liquors, which may be due to the formation of soluble vanadate. Traces of manganese were found in decreasing amounts from liquors of pH 8−12, virtually due to precipitation as the corresponding hydroxide. Other impurities such as cadmium and arsenic were found in trace amounts in all liquors.

The effects of pH of coprecipitation and annealing temperature on the characteristics of the produced powders were studied. The XRD, SEM, and vibrating sample magnetometer (VSM) were utilized as characterization tools.

Investigation of the chemical composition of the synthesized ferrite using an X-ray fluorescence spectrometer (XRF) was performed as the prepared materials are not completely soluble in various dissolving media. The synthesized ferrite that coprecipitated at pH 12 and annealed at 1000 °C was investigated using the XRF spectrometer, and the results are shown in Figure 5. The chart shows the existence of the main metal constituent of the prepared ferrite with the composition somewhat closer to the prepared Zn0.6Cu0.3Pb0.1Fe2O4. The spectra show only the main elements, and the minor elements did not clearly appear in such a technique.

II.III.2. XRD Investigation. XRD patterns of zinc−copper−lead ferrite (Zn0.6Cu0.3Pb0.1Fe2O4) nanocrystalline structures obtained from Fe3+, Zn2+, Cu2+, and Pb2+ ions coprecipitated at pH 8, 10, and 12 are shown in Figures 6−8, respectively.

Analysis of Figure 6 indicates that coprecipitation at pH 8 and subsequent calcination at 600 °C produces spinel ferrite (JCPDS #77-0012) as the dominant phase. Diffraction peaks at 2θ of 30.02, 35.35, 42.99, 53.21, 56.88, 62.40, and 73.73° correspond to spinel ferrite of diffraction planes (220), (311), (400), (422), (511), (440), and (533), respectively. Moreover, a cubic α-Fe2O3 (JCPDS #89-0599) is identified as a

![Figure 5. XRF spectra of the synthesized Zn0.6Cu0.3Pb0.1Fe2O4 coprecipitated at pH 12 and annealed at 1000 °C.](https://dx.doi.org/10.1021/acsomega.0c03426)

![Figure 6. XRD charts of the prepared Zn0.6Cu0.3Pb0.1Fe2O4 at pH 8.0.](https://dx.doi.org/10.1021/acsomega.0c03426)
secondary phase. Diffraction planes at 2θ values 24.15, 33.16, 35.64, 49.46, and 54.06, correspond to the diffraction planes (012), (104), (110), (024), and (116), which denote the presence of the α-Fe₂O₃ phase. Further to this, annealing at temperatures higher than 600 °C had a great effect on the crystallization and interaction of iron and zinc–cupric–lead phases, where the hematite phase decreases with the increasing intensity of the spinel ferrite phase. For annealing temperature from >600 to 1000 °C, an increase in the peak intensity of Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ and a decrease in those of α-Fe₂O₃ are observed. Peaks of a single phase of Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ spinel ferrite are obtained after annealing at 1100 °C. All peaks match with the corresponding spinel phase database (JCPDS #77-0012). Sharp and intense peaks observed at an annealing temperature of 1100 °C indicate fine crystalline cubic Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ spinel ferrite (Figures 7 and 8).

These findings indicated that a single phase, impurity-free nanocrystalline cubic Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ ferrite powders can be synthesized using the coprecipitation route. Figures 6–8 indicate that coprecipitation at a higher pH value such as 10 and 12 favor the formation of cubic spinel ferrite, especially at low annealing temperatures. This can be noticed from the major peaks of Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ and minor peaks of the α-Fe₂O₃ phase. However, a single phase of Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ is also obtained at 1100 °C. In general, the high-intensity and sharp peak XRD patterns suggested that annealing at 1100 °C is suitable for the synthesis of highly crystalline Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ single phase from the coprecipitated Fe, Zn, Cu, and Pb composite material, within the studied pH range from 8 to 12.

The average crystallite size of the Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ phase was estimated by applying Debye–Scherrer equation

\[ D_{\text{XRD}} = \frac{n\lambda}{\beta \cos \theta} \]  

where \( \theta \) is the Bragg angle, \( n \) is the Scherrer constant, and \( \beta \) is the full width at half-maximum of the most intense diffraction peak. Figure 9 shows that the crystalline size of Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ powders was found to increase with the increasing annealing temperature, from 600 to 1100 °C, for all studied coprecipitation pH values (8, 10, and 12). Increasing crystallite size with increasing annealing temperature can be attributed to grain development and reduction of internal stress. For samples prepared at pH 8, the crystalline size value increased from 26.6 nm for samples annealed at 600 °C to 105.7 nm for samples annealed at 1100 °C. The average crystallite size decreases with the increasing pH during coprecipitation. The crystalline size of the Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ ranges from 18.5 to 90.8 nm for samples prepared at pH 10, while it ranges from 18.7 to 87.1 nm for samples prepared at pH 12. The variation of the crystalline size with pH is explained on the basis of crystal growth. The obtained results clearly indicate that both the annealing temperature and coprecipitation pH play a role in determining the crystalline size of the prepared Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ powders.

The lattice parameter "a" for all of the synthesized cubic Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ nanocrystalline powder was calculated for the most intense (311) peak using the following formula

\[ a = d_{311}(h^2 + k^2 + l^2)^{0.5} \]  

Figure 10 and Table 5 show the variation of the lattice parameter of the prepared nanocrystalline powders,
The preference of Zn$^{2+}$ ions for the tetrahedral coordination gives rise to a normal cubic spinel structure, where tetrahedral sites are smaller than those of the octahedral ones since the ionic radius of Zn$^{2+}$ is larger than that of Fe$^{3+}$. Substitution of Fe$^{3+}$ cations by Zn$^{2+}$ cations in the tetrahedral sites at basic pH expands the normal spinel structure and hence the lattice parameter increases.

Scanning Electron Microscopy Analysis. SEM analysis of the morphology of Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$ powders obtained from the precipitated precursors at pH 8 and pH 12 is shown in Figures 11 and 12. The morphology of precursors annealed at 1000 °C is shown in Figure 11a–d, while the morphology of precursors annealed at 1100 °C is shown in Figure 12a–d. The annealing temperature has a significant effect on the morphology of the prepared powders. At 1000 °C (Figures 11a,b and 12a,b), powders feature microstructures of small and moderately large cubic particles. This indicates that the annealing temperature was inadequate for the complete formation of a perfect crystalline structure. The existence of small grains can be attributed to no coarsened hematite existing at this annealing temperature, which is in good agreement with previous investigations.43–45 With increasing annealing temperature to 1100 °C, Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$ samples have a crystalline microstructure with a regular cubic structure (Figures 11c,d and 12c,d). The microstructure becomes clear and homogeneous with a larger grain size than that detected at 1000 °C. It is found that some grains are semifused, forming larger grains, leading to the formation of microporous grains. These images also show that the precipitation pH has a significant influence on the morphology of the synthesized Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$. The morphology of the particles that precoprecipitated at pH 8 has more agglomerations and are more porous than particles that coprecipitated at pH 12.

Magnetic Properties. Magnetic properties of Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$ powders were investigated under an applied field up to 20 Koe at ambient temperatures. Figures 13–15 show the $M$–$H$ hysteresis curves of samples annealed at 600, 800, 1000, and 1100 °C and coprecipitated at pH 8, 10, and 12. The coercivity ($H_c$) and saturation magnetization ($M_s$) values of these powders are presented in Table 6. In general, Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$ powders can be referred to as soft magnetic materials due to their very low coercivity and deviation from the rectangular form. In all cases, $M_s$ gradually increases with the annealing temperature. The magnetization of the produced ferrite steadily increases with the increasing temperature from 600 to 1100 °C. This behavior can be explained to be mainly due to the conversion of the phase composition and the change in the crystalline size, in particular at low annealing temperatures. The Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$ phase contents and the crystalline size increase with the annealing temperature. Low annealing temperatures gave lower $M_s$, owing to the presence of hematite ($\alpha$-Fe$_2$O$_3$)—weak canted ferromagnet phase—as indicated by XRD analysis (Figures 5–7). The results also demonstrate that $M_s$ increases substantially with increasing coprecipitation pH, especially at low annealing temperatures (600 and 800 °C). At 600 °C, $M_s$ increases from 25.05 emu/g at pH 8 to 29.8 emu/g at pH 12. This improvement is linked to the phase growth of Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$. As explained before, coprecipitation at higher pH values favors the formation of cubic spinel ferrite.

Table 5. Variation of the Crystallite Size, Lattice Parameter, and Unit Cell Volume of Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$ Powders at Different Annealing Temperatures and Coprecipitation pH

| pH  | temperature (°C) | crystallite size, $D_{hkl}$ (nm) | lattice constant, $a_0$ (Å) | unit cell volume, V (Å$^3$) |
|-----|-----------------|---------------------------------|-----------------------------|-----------------------------|
| 8   | 600             | 26.6                            | 8.40288                     | 593.31                      |
| 800 | 71              | 8.40506                         | 593.78                      |
| 1000| 98.1            | 8.40277                         | 593.29                      |
| 1100| 105.7           | 8.40025                         | 592.76                      |
| 10  | 600             | 18.5                            | 8.40502                     | 593.77                      |
| 800 | 43.7            | 8.41504                         | 595.89                      |
| 1000| 86.2            | 8.41106                         | 595.05                      |
| 1100| 90.8            | 8.40801                         | 594.40                      |
| 12  | 600             | 18.7                            | 8.41428                     | 595.73                      |
| 800 | 40.4            | 8.42018                         | 596.99                      |
| 1000| 82.5            | 8.41704                         | 596.32                      |
| 1100| 87.1            | 8.41607                         | 596.11                      |

Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$, as a function of pH of coprecipitation and the annealing temperature. The results indicate that the lattice parameter is strongly affected by the annealing temperature. Values of the lattice parameter increase with the increasing annealing temperature up to 800 °C, which is compatible with the large increase of spinel ferrite formation and decrease of secondary impurities at this temperature.19 Above 800 °C and up to 1100 °C, a smooth decrease of the lattice parameter is observed.

Cation distribution in Zn–Cu ferrite is derived from an inverse spinel arrangement of CuFe$_2$O$_4$ and normal nonmagnetic spinel arrangement of ZnFe$_2$O$_4$. In CuFe$_2$O$_4$, half of Fe$^{3+}$ fills the octahedral sites (B sites) preferentially, and the other half fills the tetrahedral sites (A sites). In contrast, nonmagnetic Zn$^{2+}$ in ZnFe$_2$O$_4$ fills the tetrahedral sites preferentially.20,41 The reduction in the lattice parameter with annealing temperature is due to the difference in ionic sizes. The unit cell must compress when ions are replaced by smaller ionic radius ones.42 As such, with increasing occupancy of Fe$^{3+}$ in A and B sites, the lattice parameter decreases since the ionic radius of Fe$^{3+}$ (0.67 Å) is smaller than that of both Zn$^{2+}$ (0.83 Å) and Cu$^{2+}$ (0.76 Å). On the other hand, an increase of the lattice parameters with the increase of pH from 8 to 12 suggests that the normal degree of the spinel structure becomes remarkable when the synthesis is performed in a strong basic medium.

The magnetization ($M_s$) increases with the annealing temperature. Low annealing temperatures gave lower $M_s$ owing to the presence of hematite ($\alpha$-Fe$_2$O$_3$)—weak canted ferromagnet phase—as indicated by XRD analysis (Figures 5–7). The results also demonstrate that $M_s$ increases substantially with increasing coprecipitation pH, especially at low annealing temperatures (600 and 800 °C). At 600 °C, $M_s$ increases from 25.05 emu/g at pH 8 to 29.8 emu/g at pH 12. This improvement is linked to the phase growth of Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$. As explained before, coprecipitation at higher pH values favors the formation of cubic spinel ferrite.
especially at low annealing temperatures, thus increasing $M_s$. The coercivity, $H_c$, also increases from 600 to 800 °C due to the presence of hematite impurities and decreases above 800 °C with annealing temperature due to the phase evolution as well as the growth of the grain size of Zn$_{0.6}$Cu$_{0.3}$Pb$_{0.1}$Fe$_2$O$_4$.46,47

II. IV. Leaching Stability of Prepared Ferrites. Leaching stability tests of the ferrite synthesized by precipitation from the leach liquor at pH 12 and annealed at 1000 °C was carried out at different hydrochloric acid concentrations (5, 10, and 20%) at room temperature of 25 °C and at 50 °C for 60 min, and the results are listed in Table 7. It was revealed from the results that the leaching of metals was noticeably low at low temperatures and acid concentrations and slightly increased with the increase of these conditions. The ratios of dissolved metals were almost stoichiometric, especially at higher acid concentrations of 20%. The good stability of the prepared ferrite indicates the possibility of its application in diverse areas.

II. V. Cost–Benefit Analysis (CBA) and Assessment. As is shown in Figure 1b, the sequence of operations is proposed, including acid leaching of ROM ore and cyanidation of leach residue as main digestion operations. Valuable magnetic ferrite is produced from the acid leach liquor using the coprecipitation followed by calcination. In terms of mass balance, the Al Amar ore lacks Fe to synthesize stoichiometric ferrite. Ferric chloride was added to the acid leach liquor prior to ferrite precipitation to raise the Fe content to reach the
targeted molar ratios of Fe/Zn/Cu/Pb to be 2:0.6:0.3:0.1. In the real process, other iron candidates such as iron scrap can be examined. However, the effect of contamination with impurities should be addressed.

Preliminary cost–benefit analysis may provide a general image of the possible economic feasibility of the proposed sequence of operations. Table 8 presents a preliminary estimation of direct cost benefit based on 1 t ROM ore processed, excluding capital cost. Assumptions are based on material balance and prices mostly caught from bulk production manufacturers. For each 1 t ore processed, the approximate cost of consumed materials, i.e., ROM ore, HCl (36%), FeCl₃, NaCN, and NaOH, is $1063.3, and the approximate price of produced materials, i.e., gold and magnetic ferrite, is $3133.6. Therefore, an approximate benefit from material consumption and production of $2070.3 is expected based on 1 ton ore processed. Mining, processing, and labor costs are suggested to be about 60% of the materials benefit. This will cost $1242.2. Based on this preliminary cost estimation, a final profit margin of $828.1 will be gained for each 1 ton ore processed.

In the conventional process, almost all iron, zinc, and lead are stockpiled, causing environmental risk. In contrast, the proposed process utilizes these metals for the production of valuable magnetic ferrite. Acid leaching brought most of these metals into solution. The depleted leach liquor after coprecipitation shows traces of heavy metal contents. Toxic heavy metals such as lead, cadmium, and arsenic were almost not found in the spent leach liquor.

### III. CONCLUSIONS

This study presents a novel redesigned process flowsheet of Al Amar gold ore to maximize its profit margins through the production of valuable magnetic ferrite and addresses drawbacks of lost gold and metallic values in the final residue. Pretreatment of the ore by acid leaching produced valuable metallic leachate rich in copper, zinc, lead, and iron, leaving stripped gold unattacked for subsequent cyanidation. Roasting the ore at 650 °C and subsequent leaching in boiling 20% HCl provides <84% of Zn, Cu, Pb, and Fe to the solution and leaves the gold in the residue. A high gold recovery of 93% was achieved from leach residue by cyanidation. In leach liquor, the natural mole ratios of the dissolved metals were adjusted to 0.6, 0.3, 0.1, and 2.0, respectively, by adding a small amount of ferric chloride. A valuable nanocrystalline ferrite Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ was obtained from the filtrate by coprecipitation followed by heat treatment. The targeted impure phase was obtained at 600 °C, and a pure and highly crystalline single phase was obtained at 1100 °C. The crystalline size ranges from 18 to 105 nm at 600−1100 °C. The produced powder at pH 12 was found to have the finest crystalline size. Morphological analysis shows that Zn₀.₆Cu₀.₃Pb₀.₁Fe₂O₄ samples annealed at 1100 °C have uniform cubic structures with crystalline microstructures. The
produced ferrite powders can be considered as soft magnetic materials. A preliminary cost analysis based on 1 ton ore processed shows a promising approximate profit. These results demonstrate that this method leads to high gold recovery and production of valuable magnetic ferrite, paving the way for further feasibility studies of the proposed flowsheet for large-scale applications in mining processes. A preliminary cost–benefit analysis showed a promising benefit margin reaching USD828 based on 1 ton ore processed.

**IV. EXPERIMENTAL SECTION**

**IV.I. Materials.** A 20 kg sample of ground ROM of Al Amar gold ore (100%-100 mesh, 73%-200 mesh) was collected from the mine site and processing plant located to the West of Riyadh city, Saudi Arabia. The sample was thoroughly homogenized and divided several times to obtain a representative sample. The chemical composition of Al Amar ROM is presented in Table 1. All used chemicals were of pure analytical grade.

**IV.II. Roasting of Ore.** Samples of ground ROM, a 100 g each, were placed in porcelain crucibles and roasted in static air using a muffle furnace at 650 °C and 800 °C for 4 h, and then allowed to cool in air. The roasted samples were crushed and ground using a manual agate mortar and kept in sealed plastic bags until further use in leaching experiments and XRD analyses.

**IV.III. Acid Leaching.** Acid leaching experiments were carried out in a 1000 cm³ Pyrex three-necked glass reactor, fitted with a reflux condenser, a mechanical agitator, and a thermometer. Leaching solutions were prepared by diluting concentrated hydrochloric or sulfuric acid to the desired concentrations with deionized water (DW). A 50 g of roasted ROM sample and a 300 cm³ of leaching solution were added to the reactor placed in a thermostatically controlled glycerol/water bath. The slurry was stirred at 500 rpm and heated to the desired boiling temperature for 6 h. Leaching experiments in concentrated sulfuric acid were carried out in a 1000 cm³ conical flask reactor placed on a hot plate magnetic stirrer and fitted with a reflux condenser. The slurry was allowed to cool down and then filtered off using Whatman filter paper at atmospheric pressure. The filter cake was washed several times with DW until the wash liquor approach near neutrality. The washed cake was dried at 100 °C for 24 h and then kept in sealed plastic bags for further use in gold extraction experiments. The filtrate and wash liquor were mixed and kept in sealed bottles for further use in chemical analysis and coprecipitation procedures. A stock solution at the desired optimum conditions was prepared by repeating several leaching experiments.

The leaching stability experiments of synthesized ferrites were performed following procedures similar to those applied in acid leaching of ore, where 0.5 g of ferrite is mixed with 50 cm³ of leaching medium in a 100 cm³ reactor.

**IV.IV. Chemical Analysis.** The volume of the leaching solution was measured and a 1 cm³ sample was taken, diluted 10 times with DW, and chemically analyzed using inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin Elmer Optical Emission Spectrometer 2100 DV). A multielement standard solution (Perkin Elmer) was used for calibration. The dissolved contents of metals were determined, and the percentage extraction of each metal was calculated to the reactor placed in a thermostatically controlled glycerol/water bath. The slurry was stirred at 500 rpm and heated to the desired boiling temperature for 6 h. Leaching experiments in concentrated sulfuric acid were carried out in a 1000 cm³ conical flask reactor placed on a hot plate magnetic stirrer and fitted with a reflux condenser. The slurry was allowed to cool down and then filtered off using Whatman filter paper at atmospheric pressure. The filter cake was washed several times with DW until the wash liquor approach near neutrality. The washed cake was dried at 100 °C for 24 h and then kept in sealed plastic bags for further use in gold extraction experiments. The filtrate and wash liquor were mixed and kept in sealed bottles for further use in chemical analysis and coprecipitation procedures. A stock solution at the desired optimum conditions was prepared by repeating several leaching experiments.

**IV.V. Extraction of Gold.** Extraction of gold was performed in an open 500 cm³ sintered Pyrex conical flask reactor fixed in an electrical horizontal shaker. After acid leaching, the remaining dried cake of Al Amar ROM was carefully placed in the reactor and a corresponding volume of 0.01 M sodium hydroxide solution was added to adjust the pH to 11 and the solid/liquid ratio to 1:2. A weighed amount of sodium cyanide was added to adjust its concentration to 0.05, 0.1, 0.15, and 0.2%. The resulting slurry was shaken at 480 rpm for 24 h at room temperature (25 ± 2 °C). After the extraction time had elapsed, the slurry was filtered and the residue was washed several times with DW. The filtrate and washed liquor were mixed, the volume was measured, a 1 cm³ sample was taken, diluted 10 times with DW, and directly analyzed for gold by ICP-OES. The cyanidation residue was dried at 100 °C for 24 h, and the gold content was measured following aqua regia digestion and the ICP-OES technique.

**IV.VI. Synthesis of Ferrite.**

**IV.VI.I. Coprecipitation.** The targeted ferrite was prepared from the acid leach liquor of Al Amar ore by the coprecipitation technique. The mole ratios of the metallic constituents in the leach liquor was adjusted to the

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**Table 7. Leaching Stability Test of the Synthesized Ferrite at Different Conditions**

| HCl concentration (%) | 25 °C leaching (%) | 50 °C leaching (%) |
|-----------------------|--------------------|--------------------|
|                       | Zn     | Cu    | Pb    | Fe    | Zn     | Cu    | Pb    | Fe    |
| 5                     | 1.3    | 1.1   | 1.3   | 0.9   | 3.8    | 3.7   | 3.9   | 1.9   |
| 10                    | 4.6    | 4.2   | 4.7   | 3.5   | 9.8    | 10.0  | 10.7  | 8.5   |
| 20                    | 7.4    | 7.3   | 7.5   | 7.5   | 15.7   | 15.5  | 15.7  | 15.8  |

**Table 8. Preliminary Estimation of Cost–Benefit Analysis (CBA) (1 Ton ROM Ore Bases)**

| Material            | Amount | Unit | Unit Price (US$) | Price (US$) |
|---------------------|--------|------|------------------|-------------|
| ROM ore             | 1 ton  |      | 450.0/ton        | 450.0       |
| HCl (36%)           | 3.33   | metric ton | 120.0/ton    | 400.0       |
| FeCl₃               | 0.44   |      | 480.0/ton        | 211.0       |
| NaCN                | 1 kg   |      | 1200.0/ton       | 1.2         |
| NaOH                | 0.4 kg |      | 2800.0/ton       | 1.1         |
| Total cost of consumed materials (A) |        |      | 1063.3          |             |
| Gold                | 6.02 g |      | 62.06/g         | 373.6       |
| Magnetic ferrite    | 0.69 ton |      | 4000.0/ton      | 2760.0      |
| Total price of produced materials (B) |        |      | 3133.6          |             |
| Benefit (B–A)       |        |      | 2070.3          |             |
| Operation cost      |        |      | 1242.2          |             |
| Total profit margin |        |      | 828.1           |             |

*Excluding capital cost. *Personal communication with Ma’aden company officials, KSA. *Bulk production from manufacturers, Web based (e.g., https://dir.indiamart.com/impcat/hydrochloric-acid.html). *Published daily gold price, Web based (e.g., https://www.monex.com/gold-prices/). *Internal joint research project between Taif University and SABIC company, KSA.

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intended values of 0.6:0.3:0.1:2.0 of zinc/copper/lead/iron, respectively, by adding a precalculated amount of ferric chloride (FeCl₃·6H₂O, Sigma-Aldrich). Three samples of the leach liquor, 300 cm³ each, were then taken and their pH values were adjusted to 8, 10, and 12, respectively, using a 5 M sodium hydroxide solution. The pH was measured using a benchtop pH meter (Fisherbrand FE150). The slurries were kept overnight on a magnetic stirrer at room temperature to complete the metal precipitation and then filtered off on Whatman filter paper. The solid precipitates were washed with DW and acetone, separated, dried at 100 °C for 24 h, and kept in sealed plastic bags. The corresponding volumes of barren filtrates were measured and 1 cm³ samples were taken for chemical analysis by ICP-OES.

IV.VIII. Heat Treatment. A 2.5 g of sample of each dried precipitate was placed in a ceramic crucible, annealed at the required temperatures (ranging from 600 to 1100 °C) in a muffle furnace for 4 h in a static air atmosphere, and then cooled gradually to room temperature. The obtained solids were crushed gently with a spatula and kept in sealed plastic bags for characterization.

IV.VII. Characterization of Ferrite. Identification of the crystalline phases of the different annealed samples was performed using XRD. The XRD measurements were carried out at room temperature using a Brucker AXS D8 diffractometer operating with diffracted beam graphite monochromators (Cu Kα with λ =1.5406 Å) at 40 kV and 40 mA. The morphologies of synthesized powders were characterized by SEM, JEOL, and JSM-5400. The magnetic properties of the synthesized materials were determined at room temperature using a vibrating sample magnetometer (VSM; 9600-1 LDJ) in a maximum applied field of 7 kOe. Saturation magnetization (Mₛ) and coercivity (Hᵥ) were determined from the obtained hysteresis loops.

The chemical composition of synthesized samples was also investigated by an energy-dispersive X-ray fluorescence (EDXRF) spectrometer (Thermo Fisher Scientific, model: Quan’t X) using the Uniquant standardless method and the free powder technique. The ground sample was placed in a preassembled sample plastic cup (40 mm diameter × 38.4 mm height) and covered with a polypropylene support thin films 3.6 μm thickness (Chemplex industries Inco).

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Notes
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■ REFERENCES

(1) Mahmoud, M. H.; Awad, H. M.; Elhabib, O. A. Gold leaching from a Saudi ore by the nonpolluting thiosulfate process. Physicochem. Probl. Miner. Process. 2015, 51, 59–72.
(2) Mahmoud, M. H.; Awad, H. M.; Altalhi, T. Microanalysis study of Al-Amar rock and leaching behavior of its tailings for recovery of gold and silver. Physicochem. Probl. Miner. Process. 2018, 54, 527–537.
(3) Mahmoud, M. H.; Awad, H. M. Improved recovery of gold and silver from thiosulfate solution on activated carbon in presence of ammonium persulfate. Physicochem. Probl. Miner. Process. 2019, 55, 1271–1285.
(4) Liu, X.; Li, Q.; Zhang, Y.; Jiang, T.; Yang, Y.; Xu, B.; He, Y. Improving gold recovery from a refractory ore via Na₂S₅O₇ assisted roasting and alkaline Na₂S leaching. Hydrometallurgy 2019, 185, 133–141.
(5) Almeida, M. Leaching of a gold bearing partially roasted sulphide. Laboratory scale studies. Mater. Res. 2001, 4, 305–314.
(6) Adams, M. D. Gold ore processing: Project Development and Operations; Elsevier, 2016.
(7) Celep, O.; Ibrahim, A.; Haci, D.; Vicil, M. Characterization of refractory behaviour of complex gold/silver ore by diagnostic leaching. Trans. Nonferrous Met. Soc. China 2009, 19, 707–713.
(8) Marsden, J.; House, I. The Chemistry of Gold Extraction; SME, 2006.
(9) Dutrizac, J. The leaching of sulphide minerals in chloride media. Hydrometallurgy 1992, 29, 1–45.
(10) Nyamjargal, L.; Batdemberel, G.; Burmaa, G.; Burmaa, D. Effect of Roasting Temperature for Copper Leaching of Sulfide Concentrate by Combined Methods. Open J. Appl. Sci. 2018, 8, 545–553.
(11) Celep, O.; Ibrahim, A.; Doğan, P.; Yves, T. Implementation of sodium hydroxide pretreatment for refractory antimonial gold and silver ores. Hydrometallurgy 2011, 108, 109–114.
(12) Saeed, I.; Celep, O.; Pakung, D.; Yves, T. Influence of potassium hydroxide pretreatment on the extraction of gold and silver from a refractory ore. Hydrometallurgy 2014, 146, 64–71.
(13) Celep, O.; Ibrahim, A.; Haci, D. Improved gold and silver extraction from a refractory antimony ore by pretreatment with alkaline sulphide leach. Hydrometallurgy 2011, 105, 234–239.
(14) Pereira, A. C.; da Silva Borges Barbosa, V. Effectiveness acidic pre-cleaning for copper-gold ore. REM, Int. Eng. J. 2017, 70, 445–450.
(15) Li, Q.; Zhang, Y.; Liu, X.; Xu, B.; Yang, Y.; Jiang, T. Improvement of gold leaching from a refractory gold concentrate calcine by separate pretreatment of coarse and fine size fractions. *Minerals* 2017, 7, No. 80.

(16) Shwetambaram, A.; Vakil, Z. Synthesis of zinc-copper nano-ferrite and characterization of their structural, electrical and magnetic behaviors. *Int. J. ChemTech Res.* 2014, 6, 2207–2209.

(17) Singh, S.; Goswami, N.; Kataly, S. C. In *Nanostructured Zn-Cu Ferrite: Structural, Magnetic Properties and Application*, AIP Conference Proceedings; AIP Publishing LLC, 2018.

(18) Dhiwasar, A. T.; Sundararajan, M.; Sakhthivel, P.; Dash, Chandra Sekhar.; Yuvaraj, S. Microwave-assisted combustion synthesis of pure and zinc-doped copper ferrite nanoparticles: Structural, morphological, optical, vibrational, and magnetic behavior. *J. Phys. Chem. Solids* 2020, 138, No. 109257.

(19) Hessien, M. M.; Mersal, Gaber A. M.; Mohsen, Q.; Alosaimi, Diyayel. Structural, magnetic and sensing properties of lanthanum ferrite via facile sol gel oxide precursor route. *J. Mater. Sci.: Mater. Electron.* 2017, 28, 4170–4178.

(20) Ahmed, M. A.; Ateia, E.; Salah, L. M.; El-Gamal, A. A. Structural and electrical studies on La1–xSrxMnO3 substituted Ni–Zn ferrites. *Mater. Chem. Phys.* 2005, 89, 310–321.

(21) Camacho-González, M. A.; Quezada-Cruz, M.; Cerón-Montes, G. I.; Ramírez-Ayala, M. F.; Hernández-Cruz, L. E.; Garrido-Hernández, A. Synthesis and characterization of magnetic zinc-copper ferrites: Antibacterial activity, photodegradation study and heavy metals removal evaluation. *Mater. Chem. Phys.* 2019, 236, No. 1211080.

(22) Kmita, A; Lachowicz, D.; Złotkowska, J.; Gajewska, M.; Szczepańska, W.; Kuciakowski, J.; Zapotoczny, S.; Sikora, M. One-step synthesis of long term stable superparamagnetic colloidal of zinc ferrite nanorods in water. *Materials* 2019, 12, No. 1048.

(23) Anjaneyulu, T.; Murthy, P. N.; Rafi, S. M.; Bademiya, S.; John, G. S. Effect on magnetic properties of zinc doped nano ferrites synthesized by precursor method. *Int. Lett. Chem., Phys. Astron.* 2013, 14, 37–43.

(24) Jain, A.; Baranwal, R. K.; Bharti, A.; Vakil, Z.; Prajapati, C. S. Study of Zn-Cu ferrite nanoparticles for LPG sensing. *Sci. World J.* 2013, 1, 7–1–7.

(25) Pan, W.; Gu, F.; Qi, K.; Liu, Q.; Wang, J. Effect of Zn substitution on morphology and magnetic properties of CuFe2O4 nanofibers. *Mater. Chem. Phys.* 2012, 134, 1097–1101.

(26) Mubarak, T. H.; Hassan, K. H.; Ali, Z. M. Preparation and study structure properties of Zinc-Copper ferrite (ZnOx Cu1−xFe2O4) nanoparticles. *IOSR J. Appl. Phys.* 2017, 9, 8–12.

(27) Jesenthirani, V.; George, M.; Jeyaraja, B.; Dayalana, A.; Nagaraja, K. S. Synthesis of metal ferrite (MFe2O4, M= Co, Cu, Mg, Ni, Zn) nanoparticles as humidity sensor materials. *J. Exp. Nanosci.* 2013, 8, 358–370.

(28) Narasimhan, B.; Kumar, S.; Narayanan, T. S. Synthesis of manganese zinc ferrite using ferrous pickle liquor and pyrolusite ore. *Environ. Chem. Lett.* 2011, 9, 243–250.

(29) Gao, Lihua.; Liu, Zhonggen.; Ge, Yang.; Feng, Cong.; Chu, Mansheng; Tang, Jue. Synthesis and characterization of manganese ferrite Mn3Fe5O12 from ferruginous manganese ores by multi-step roasting and magnetic separation. *Powder Technol.* 2019, 356, 373–382.

(30) Herrera, P. S.; Uchiyama, H.; Igarashi, T.; Asakura, K.; Ochi, Y.; Ishizuaka, F.; Kawada, S. Acid mine drainage treatment through a two-step neutralization ferrite-formation process in northern Japan: Physical and chemical characterization of the sludge. *Miner. Eng.* 2007, 20, 1309–1314.

(31) Bajwa, M. A.; Asif, R.; Ghulmon, M.; Retnowati, D. Y. et al. Ferrite-Based Nanoparticles Synthesized from Natural Iron Sand as the Fe3+ Ion Source. In *Nanocrystalline Materials*, IntechOpen, 2019.

(32) Celep, O.; Serbest, V. Characterization of an iron oxy/hydroxide (gossan type) bearing refractory gold and silver ore by diagnostic leaching. *Trans. Nonferrous Met. Soc. China* 2015, 25, 1286–1297.

(33) Haynes, W. M. CRC Handbook of Chemistry and Physics; CRC Press, 2014.

(34) Byrne, R. H.; Yao, W.; Luo, Y.; Miller, F. J. Complexation of Pb (II) by chloride ions in aqueous solutions. *Aquat. Geochem.* 2010, 16, 325–335.

(35) Silwamba, M.; Ito, M.; Hiroyoshi, N.; Tabelin, C.; Hashizume, R.; Chirwa, M.; et al. Recovery of Lead and Zinc from Zinc Plant Leach Residues by Concurrent Dissolution-Cementation Using Zero-Valent Aluminum in Chloride Medium. *Metals* 2020, 10, No. 531.

(36) Habashi, F. The leaching of sulfdes minerals in chloride media. *Hydrometallurgy* 1995, 38, 219.

(37) Abdel-Rehim, A. Thermal and XRD analysis of Egyptian galena. *J. Therm. Anal. Calorim.* 2006, 86, 393–401.

(38) Thao, N. T. P.; Tsujii, S.; Jeon, S.; Park, I.; Tabelin, C.; Ito, M.; Hiroyoshi, N. Redox potential-dependent chalcopyrite leaching in acidic ferric chloride solutions: Leaching experiments. *Hydrometallurgy* 2020, 194, No. 105299.

(39) Kianinia, Y.; Khalesi, M. R.; Abdollahy, M.; Hefer, G.; Senanayake, G.; Hnedkovsky, L.; Darban, A. K.; Shahbazi, M. Predicting cyanide consumption in gold leaching: a kinetic and thermodynamic modeling approach. *Minerals* 2018, 8, No. 110.

(40) Patterson, A. The Scherrer formula for X-ray particle size determination. *Phys. Rev.* 1939, 56, No. 978.

(41) Verma, S.; Chand, J.; Batoo, K. M.; Singh, M. Cation distribution and M össbauer spectral studies of MnxMn1−xNi1−y,lnFe2−3yO4 ferrites (x∼0.0, 0.05 and 0.10). *J. Alloys Compd.* 2013, 565, 148–153.

(42) Kerroum, M. A. A.; Essyed, A.; Iacovita, C.; Baaziz, W.; Ihiawakrim, D.; Mounkachi, O.; Hamedoun, M.; Benyoussef, A.; Benaissa, M.; Ersen, O. The effect of basic pH on the elaboration of ZnFe2O4 nanoparticles by co-precipitation method: Structural, magnetic and hyperthermia characterization. *J. Magn. Magn. Mater.* 2019, 478, 239–246.

(43) Hessien, M. M. Synthesis and characterization of lithium ferrite by oxide precursor route. *J. Magn. Magn. Mater.* 2008, 320, 2800–2807.

(44) Hessien, M. M.; Rashad, M. M.; El-Barawy, K.; Ibrahim, I. A. Influence of manganese substitution and annealing temperature on the formation, microstructure and magnetic properties of Mn–Zn ferrites. *J. Magn. Magn. Mater.* 2008, 320, 1615–1621.

(45) Costa, A. C. F. M.; Tortella, E.; Morelli, M. R.; Kiminni, R. H. A. G. Synthesis, microstructure and magnetic properties of Ni–Zn ferrites. *J. Magn. Magn. Mater.* 2003, 256, 174–182.

(46) Wang, H. Z.; Hai, Y. N.; Yao, B.; Xu, Y.; Shan, L.; Xu, L.; Tang, J. L.; Wang, Q. H. Tailoring structure and magnetic characteristics of strontium hexaferrite via Al doping engineering. *J. Magn. Magn. Mater.* 2017, 422, 204–208.

(47) Hessien, M. M.; El-Bagoury, N.; Mahmoud, M. H. H.; Alsaawat, M.; Alanazi, A. K.; Rashad, M. M. Implementation of La3+ ion substituted M-type strontium hexaferrite powders for enhancement of magnetic properties. *J. Magn. Magn. Mater.* 2020, 498, No. 166187.

(48) Park, I.; Tabelin, C. B.; Jeon, S.; Li, X.; Seno, K.; Ito, M.; Hiroyoshi, N. A review of recent strategies for acid mine drainage prevention and mine tailings recycling. *Chemosphere* 2019, 219, 588–606.