Improvement of Gold Leaching from a Refractory Gold Concentrate Calcine by Separate Pretreatment of Coarse and Fine Size Fractions

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Abstract: A total gold extraction of 70.2% could only be reached via direct cyanidation from a refractory As-, S- and C-bearing gold concentrate calcine, and the gold extraction varied noticeably with different size fractions. The reasons for unsatisfactory gold extraction from the calcine were studied through analyses of chemical composition, chemical phase and SEM-EDS of different sizes of particles. It was found that a significant segregation of compositions occurred during the grinding of gold ore before flotation. As a result, for the calcine obtained after oxidative roasting, the encapsulation of gold by iron oxides was easily engendered in finer particles, whilst in coarser particles the gold encapsulation by silicates was inclined to occur likely due to melted silicates blocking the porosity of particles. The improvement of gold leaching from different size fractions was further investigated through pretreatments with alkali washing, acid pickling or sulfuric acid curing-water leaching. Finally, a novel process was recommended and the total gold extraction from the calcine could be increased substantially to 93.6% by the purposeful pretreatment with alkali washing for the relatively coarse size fraction (+37 µm) and sulfuric acid curing–water leaching for the fine size fraction (−37 µm).

Keywords: refractory gold concentrate; calcine; acid pickling; alkali washing; sulfuric acid curing–water leaching

1. Introduction

Refractory gold ores have increasingly been the main source of gold production with the exhaustion of amenable gold ores. Of the 2630 tons of total world gold production in 2011, about 25% was produced from refractory gold deposits, and of the top 20 gold operations in 2011, eight were processing refractory ores [1]. Commonly, relatively high content of detrimental impurities like S (sulfur), As (arsenic) and C (carbon) occur in these refractory gold ores [2–4]. Also, gold is usually disseminated as micro-fine particles which are easily encapsulated in associated minerals, resulting in unacceptable exposure levels of gold unless undergoing ultra-fine grinding with high energy consumption. As a result, proper pretreatments are necessary to improve the leaching of gold from these refractory gold ores [5,6].

The pretreatment of oxidative roasting has always been one of the most extensively used methods in China attributing to its mature technique, high efficiency, energy conservation, etc. [7,8] Effective removal of harmful elements including S, As and C can be achieved after oxidative roasting, but the sintering phenomenon occurs inevitably even when adjusting the roasting atmosphere and lowering the roasting temperature [9]. Consequently, the oxidative roasting is often accompanied by the
secondary encapsulation of gold, which leads to the unsatisfactory extraction of gold from the calcine and thus the waste of gold resources [7,10–13].

The locked gold in calcine is commonly referred to as encapsulation by iron oxides (mainly hematite, \( \text{Fe}_2\text{O}_3 \)). Currently, the pretreatment of acid pickling (i.e., commonly using dilute sulfuric acid liquors to dissolve iron oxides) has been widely used to open the encapsulation of gold in metallurgical plants of China [14]. The acid consumption is generally high, but the damage of iron oxides is still insufficient, and so the improvement of gold extraction is rather limited [15–17]. It has been shown that about 50% of iron could be leached from a cinder of pyrite at the optimal conditions of leaching temperature 110 °C, sulfuric acid concentration 55% (\( \text{w/w} \)), and leaching time 2 h [15]. Similarly, the research of, Zhang et al. [17] indicated that the optimal leaching ratio of iron from a pyrite cinder was only 45%. In view of crystal forms of \( \text{Fe}_2\text{O}_3 \), the dissolution rates of \( \alpha\text{-Fe}_2\text{O}_3 \) and \( \gamma\text{-Fe}_2\text{O}_3 \) in sulfuric acid were also investigated and it was found that the leaching of iron from \( \alpha\text{-Fe}_2\text{O}_3 \) and \( \gamma\text{-Fe}_2\text{O}_3 \) were both rather restricted, with an iron leaching ratio of 20% and 40%, respectively [16]. Other pretreatments that include reduction roasting–acid pickling, acidic pressure pickling and sulfuric acid curing (i.e., directly using concentrated sulfuric acid to react with iron oxides under high temperatures)–water leaching were further studied to expose the locked gold [18–22]. The removal of iron oxides is enhanced to some degree by using the former two methods, but the gold extractions are still not high enough for some gold calcines. By comparison, the sulfuric acid curing-water leaching is more advantageous due to the higher damage degree of iron oxides and the simple technology [23]. The iron oxides can be transformed fully into a soluble form of rhomboclase \( \text{HFe(SO}_4\text{)}_2\cdot4\text{H}_2\text{O} \) by this pretreatment, so the effective exposure of gold can be achieved to significantly improve gold extraction [24–27].

Additionally, the gold encapsulated in gangue minerals, especially in quartz or silicate, cannot effectively be exposed during the oxidative roasting. On the contrary, a more compact structure of the silicates is apt to form after oxidative roasting, causing another secondary encapsulation of gold by silicates [28]. Brady et al. [29] researched the dissolution of silicate in neutral and basic pH solutions and found that a higher pH was beneficial to the dissolution of silicates. Therefore, it is necessary to expose the gold encapsulated in silicates through pretreatment with alkali washing [30,31].

With respect to the simultaneous encapsulation of gold by iron oxides and silicates, however, the efficient extraction of gold is nearly impossible by only sulfuric acid curing–water leaching or alkali washing. As for the distribution of gold, Paktunc et al. [32] found that gold tended to be distributed in fine-grained and inclusion-rich pyrite crystals rather than the coarse-grained crystals, and after roasting, the gold appeared to be confined to impervious bands of maghemite within iron oxide particles and to mimic the distribution of arsenic. Moreover, it was also reported that gold encapsulation in iron oxides occurred more easily in the relatively fine size fraction of calcine [13,33], but the causes for this phenomenon are still unclear. Little research has concentrated on exposing the encapsulated gold in different size fractions of the calcine.

In this paper, the particle characteristics including the chemical compositions, chemical phase and particle morphology of different size fractions of the gold concentrate and calcine were investigated systematically. On this basis, the enhancement of gold leaching from the calcine was studied by purposefully pretreating each size fraction with sulfuric acid curing-water leaching or alkali washing. Finally, an efficient process from improving gold extraction from refractory As-, S- and C-bearing gold concentrate calcine was developed based on the different predominant encapsulation phase of gold in different size fractions of the calcine.

2. Materials and Methods

2.1. Materials and Reagents

The As-, S- and C-bearing gold concentrate was a floatation concentrate from Yunnan province of China. The calcine was obtained from the gold concentrate by two-stage oxidative roasting.
Mineralogical phases of the gold concentrate and calcine were determined by quantitative X-ray diffraction (XRD) analysis, and the chemical and mineralogical compositions of them are shown in Table 1. Through optical microscopy and electron probe microanalyses and chemical analyses for different phases, the chemical phase analyses of gold in the concentrate and calcine are also presented in Table 2.

It is indicated in Table 1 that the gold concentrate had a high content of S (20.76%), As (1.62%) and C (6.95%), which are all possibly detrimental to gold leaching. Specifically, according to the chemical phase analyses of gold in the concentrate (see Table 2), the gold concentrate belongs to a refractory sulfidic carbonaceous gold ore chiefly due to the encapsulation of gold by associated sulfides (mainly pyrite and arsenopyrite) and the “preg robbing” of gold by carbonaceous matters (mainly simple substance C). After two-stage oxidative roasting, most of the S (93.84%), As (71.40%) and C (98.27%) in the gold concentrate was removed and the content of gold increased from 18.05 g/t to 22.50 g/t. In addition, the exposed gold (cyanide leachable) increased from 1.72% in the concentrate to 64.27% in the calcine. However, the enclosed gold by iron oxides increased significantly from 10.36% in the concentrate to 21.96% in the calcine, which indicated that, except the initial gold encapsulated by iron oxides, during oxidation roasting, the secondary gold encapsulation by iron oxides occurred. Meanwhile, the distribution of gold in silicates rose markedly from 0.71% in the concentrate to 11.41% in the calcine, meaning that the secondary gold encapsulation by silicates was also generated during oxidation roasting. Actually during the roasting, solid phase reactions of FeO with SiO\(_2\), Al\(_2\)O\(_3\), etc. can occur at a temperature of less than 600 °C. Together with the exothermic effect of carbon combustion, an overhigh local temperature is inclined to be caused and thereby leading to the fusion of low-melting resultants of solid-solid reactions such as fayalite and aluminosilicate, resulting in the secondary encapsulation of gold by silicates [34]. At the same time, under overhigh local temperature, the iron oxides will undergo recrystallization leading to secondary gold encapsulation by iron oxides.

### Table 1. Chemical and mineralogical compositions of gold concentrate and calcine samples/(mass fraction, %).

<table>
<thead>
<tr>
<th>Chemical Compositions</th>
<th>Au *</th>
<th>Fe</th>
<th>S</th>
<th>As</th>
<th>C</th>
<th>K(_2)O</th>
<th>CaO</th>
<th>MgO</th>
<th>Al(_2)O</th>
<th>SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate</td>
<td>18.05</td>
<td>19.60</td>
<td>20.76</td>
<td>1.62</td>
<td>6.95</td>
<td>2.10</td>
<td>4.26</td>
<td>2.00</td>
<td>6.19</td>
<td>27.68</td>
</tr>
<tr>
<td>Calcine</td>
<td>22.50</td>
<td>25.44</td>
<td>1.83</td>
<td>0.42</td>
<td>0.13</td>
<td>2.24</td>
<td>4.58</td>
<td>1.96</td>
<td>7.87</td>
<td>34.61</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineralogical Compositions</th>
<th>Arsenopyrite</th>
<th>Pyrite</th>
<th>Hematite</th>
<th>Magnetite</th>
<th>Simple Substance C</th>
<th>Dolomite</th>
<th>Gypsum</th>
<th>Quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate</td>
<td>3.48</td>
<td>38.66</td>
<td>3.23</td>
<td>0.79</td>
<td>4.37</td>
<td>15.89</td>
<td>0.18</td>
<td>27.89</td>
</tr>
<tr>
<td>Calcine</td>
<td>3.04</td>
<td>35.27</td>
<td>3.82</td>
<td>0.07</td>
<td>0.86</td>
<td>12.73</td>
<td>7.87</td>
<td>34.47</td>
</tr>
</tbody>
</table>

* Unit g/t.

### Table 2. Results of chemical phase analyses of Au in gold concentrate and calcine samples.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Exposed Gold</th>
<th>In Sulfides</th>
<th>In Iron Oxides</th>
<th>In Silicates</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate</td>
<td>0.31</td>
<td>15.74</td>
<td>1.87</td>
<td>0.13</td>
<td>18.05</td>
</tr>
<tr>
<td>Distribution</td>
<td>1.72</td>
<td>87.21</td>
<td>10.36</td>
<td>0.71</td>
<td>100.00</td>
</tr>
<tr>
<td>Calcine</td>
<td>14.46</td>
<td>0.53</td>
<td>4.94</td>
<td>2.57</td>
<td>22.50</td>
</tr>
<tr>
<td>Distribution</td>
<td>64.27</td>
<td>2.36</td>
<td>21.96</td>
<td>11.41</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The reagents used in this study, such as sodium cyanide, sodium hydroxide and sulfuric acid, were all of analytically pure grade. De-ionized water was used throughout all experiments.

#### 2.2. Experiment Methods

The simplified flow chart of manipulations is presented in Figure 1. The size grading of gold concentrate or calcine was carried out in water with screens of 200 mesh and 400 mesh, thus obtaining three particle size fractions of +75 µm (coarse), +37~−75 µm (medium) and −37 µm (fine). These
different size fractions were filtrated, dried and stored in air-tight plastic bags. The two-stage oxidative roasting of gold concentrate was conducted in a horizontal tube furnace under the optimum conditions that had been obtained in our previous studies [31], aiming to remove As in the I stage and then S and C in the II stage.

Figure 1. Simplified flow chart of the manipulations.

Before the pretreatments and cyanidation of calcines, the coarse and medium size fractions were previously dry-milled in a planetary ball mill to be \(-37 \mu m\) over 90%. The pretreatment of calcines by acid pickling or alkali washing were conducted in 1-L jacketed glass reactors each equipped with overhead mechanical stirrer (IKAWESTPCUS25), condenser and thermometer, and the reactors were connected with thermostatic water baths to control reaction temperature. The reaction conditions were liquid-solid ratio 3:1, temperature 80 °C, stirring speed 300 rpm, H\(_2\)SO\(_4\) 15% (mass fraction)/NaOH 2% (mass fraction) and time 1 h. The sulfuric acid curing-water leaching of calcines was firstly carried out in a ceramic crucible at a muffle furnace, and then the reaction product was leached by water in a 1-L beaker where pulp was stirred by a mechanical agitator. The reaction conditions of sulfuric acid curing were H\(_2\)SO\(_4\) 75% (mass fraction), excess coefficient of H\(_2\)SO\(_4\) 1.4 (ratio of the actual amount to the theoretical amount), temperature 250 °C and time 1 h. The conditions of water leaching were liquid–solid ratio 3:1, stirring speed 300 rpm, temperature 25 °C and time 2 h. Gold cyanide leaching was implemented under the conditions of liquid–solid ratio 2.5:1, temperature 25 (±0.5) °C, stirring speed 600 rpm, NaCN 0.4% (mass fraction), time 36 h and pH 11, and the pH was adjusted by the careful addition of 1.0 M NaOH solution. When the pretreatment or gold leaching test was completed, the pulp was filtered by a vacuum filter and the obtained filter residue was washed adequately.

2.3. Analytical Methods

S and C contents in the gold concentrate and calcine were determined using a high frequency IR carbon and sulfur analyzer (HW2000B, Wuxi Yingzhicheng, Wuxi, China). The other elements were all analyzed using acid digestion and an atomic absorption spectrometer (AA-6800, Shimadzu, Kyoto, Japan). The specific surface areas of mineral particles were detected by the laser particle size analyzer (Mastersize2000, Malvern Instruments Ltd., Malvern, UK). Morphological studies on the calcine were carried out with Scanning Electron Microscope coupled with Energy Dispersive Spectrometer (JSM-6360LV, JEOL Ltd., Tokyo, Japan).

Chemical phase analysis of gold is extensively adopted in China for research on gold-bearing materials, and the steps of analysis are as follows: firstly, the occurrence of gold in different phases was found out by optical microscopy and electron probe microanalyses, and then the content of gold in each phase was determined by the selective dissolving of each phase with certain chemical reagents [35,36]. The exposed gold represents that gold is leachable by direct cyanidation while the gold in sulfides, iron oxides and silicates means that gold is not cyanide leachable due to being separately locked in those associated minerals.
3. Results and Discussion

3.1. Gold Leaching from Different Size Fractions of the Calcine by Direct Cyanidation

Before and after cyanidation, the content and distribution of gold in the different size fractions of calcine and the corresponding gold extraction are listed in Table 3.

Table 3. Results of gold leaching from the different size fractions of calcine.

<table>
<thead>
<tr>
<th>Size Fraction/µm</th>
<th>Calcine</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+75</td>
<td>+37−75</td>
</tr>
<tr>
<td>Before cyanidation</td>
<td>Au content/(g/t)</td>
<td>16.85</td>
</tr>
<tr>
<td></td>
<td>Au distribution/%</td>
<td>21.84</td>
</tr>
<tr>
<td>After cyanidation</td>
<td>Au content/(g/t)</td>
<td>4.88</td>
</tr>
<tr>
<td></td>
<td>Au distribution/%</td>
<td>19.97</td>
</tr>
<tr>
<td></td>
<td>Gold extraction/%</td>
<td>72.3</td>
</tr>
</tbody>
</table>

Table 3 shows that the total gold extraction of calcine was only 70.2%, and the gold extraction differed significantly with size fraction, following the sequence of the medium (+37−75 µm) > the coarse (+75 µm) > the fine (−37 µm). The medium size fraction obtained a relatively high gold extraction of 82.6%, but the gold extractions from the coarse (72.3%) and particularly from the fine (59.7%) were both unsatisfactory. After cyanidation, for the gold in the leached residue, the gold distribution in the fine size fraction accounted for as high as 63.01% which was much higher than that in the coarse (19.97%) and the medium (17.02%).

3.2. Particle Characteristics of the Gold Concentrate and Calcine

Aiming to clarify the gold leaching behaviors from various size fractions of the calcine, the distribution of main chemical compositions including SiO$_2$, Al$_2$O$_3$, C, S, Fe and Au, and the chemical phase of gold and the particle morphology were further studied for the gold concentrate and calcine.

3.2.1. Distribution of Main Chemical Compositions in the Different Size Fractions of Gold Concentrate and Calcine

In the concentrate, as indicated in Table 4, the allocation of coarse size fraction (20.91%) was close to the medium size fraction (23.93%), while up to 55.16% of particles were distributed in the fine size fraction. The main chemical compositions of gold concentrate are depicted in Figure 2. The content of Al$_2$O$_3$ fluctuated slightly in different size fractions, but that of SiO$_2$ in the coarse (40.95%) and medium (35.00%) size fraction were both much higher than the fine size fraction (19.47%). Additionally, C, S, Fe and Au were prone to being concentrated in finer size fractions. The reasons for the above primarily lie in two aspects. On the one hand, the gold concentrate has undergone an ore grinding process before flotation, so selective grinding easily occurs attributing to the grindability difference especially among sulfide ore (mainly pyrite and arsenopyrite), carbonaceous matter (mainly simple substance C) and quartz (or silicate) [37]. With relatively low hardness, pyrite, arsenopyrite and simple substance C are ground in priority and easily segregated into relatively fine fractions. Meanwhile, quartz (or silicate) whose hardness is high is inclined to be segregated into the relatively coarse size fractions. On the other hand, 87.21% of gold in the concentrate is encapsulated in sulfide minerals (see Table 2) and the gold will still be associated with the iron oxides generated from the oxidative roasting of sulfide minerals, so the simultaneous segregation of gold into finer mineral particles also occurs.
It can be seen in Table 1 that most S and C were removed during the oxidative roasting of concentrate. Also, the ignition loss is mainly determined by the content of S and C. Thus, it is found from Figure 2 that the content of S and C in the different size fractions of calcine all declined to quite low levels. Accordingly, the content of the other compositions in calcine all rose to some extent comparing with the concentrate. Similar to the concentrate, in the calcine the coarse and medium size fractions always had much higher content of SiO$_2$ whilst the fine size fraction had obviously higher content of Fe and Au. Additionally, due to the removal of higher content of S and C in the fine particles during roasting, we can see clearly from Table 4 that the distribution of fine size fraction decreased from 55.16% for the concentrate to 42.58% for the calcine, meaning that the overall size of mineral particles became larger after the oxidative roasting. Nevertheless, the measured specific surface area grew obviously from 1473 cm$^2$/g of the concentrate to 2565 cm$^2$/g of the calcine, owing to the release of S, C and As from the mineral matrix in a volatile form like SO$_2$, CO$_2$ and As$_2$O$_3$. Hence, a porous structure of calcine particle can be attained and it is beneficial for the exposure of gold.

3.2.2. Chemical Phase Analysis of Gold in the Different Size Fractions of Calcine

For the calcine, the gold phase in different size fractions was also studied by chemical phase analysis and the result is shown in Figure 3.

As seen from Figure 3, after oxidative roasting the distribution of leachable gold in the medium size fraction (79.48%) was clearly higher than that in the coarse (68.59%) and fine (51.34%) fractions, which is in accordance with the gold leaching results in Table 3. For the locked gold, it is explicit that in the fine size fraction 36.97% of gold primarily occurred in iron oxides, which is much higher than the gold encapsulated in silicates and sulfides (7.93% and 3.77%). In contrast, in the coarse size fraction, more gold was encapsulated in silicates (20.59%) than in iron oxides (9.7%) and sulfides (1.32%).

Table 4. The distribution and specific surface area of different size fractions/(mass fraction, %).

<table>
<thead>
<tr>
<th>Gold Ore Type</th>
<th>Specific Surface Area/(cm$^2$/g)</th>
<th>Size Fraction Distribution/Mass Fraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>+75 μm</td>
</tr>
<tr>
<td>Concentrate</td>
<td>1473</td>
<td>20.91</td>
</tr>
<tr>
<td>Calcine</td>
<td>2565</td>
<td>29.10</td>
</tr>
</tbody>
</table>

Figure 2. Main chemical compositions of the different size fractions.
was relatively compact than the fine particle. Additionally, the EDS spectra of the calcine particles, possibly blocked by melted silicates during oxidative roasting to hinder the gold leaching. Meanwhile, it was more likely for fine particles to form the encapsulation of gold by iron oxides.

Further partial enlargement (amplification ×10,000) of the marked area in Figure 4a,d is presented in Figure 4b,e, respectively. It is clearly indicated that the surface structure of the coarse particle was in Figure 4c,f, and the quantitative EDS analysis (see Table 5) indicate that the coarse particle contained in Figure 4b,e, respectively. It is clearly indicated that the surface structure of the coarse particle was

This further confirms the composition segregation phenomenon. It has been ascertained in the concentrate that 87.21% of gold is enclosed in iron-containing sulfides and 10.36% of gold in iron oxides. Hence, with an intimate relationship between Au and Fe, most gold will occur in iron oxides in the calcine after oxidative roasting. Since there is an obvious excess of Fe (i.e., iron oxides) over SiO₂ in the fine particles of calcine, except the original enclosed gold by iron oxides, it is inevitable that the secondary encapsulation of gold by iron oxides occurs attributing to the recrystallization of iron oxides. Namely, the occurrence of encapsulated gold in fine particles is mainly in iron oxides. The situation in the coarse size fraction is quite different arising from the composition segregation. Much higher content of SiO₂ than Fe in the coarse size fraction possibly results in the formation of low-fusing fayalite as well as other silicates under overhigh local temperatures. Consequently, the pores of iron oxides are blocked by the melted silicates and the gold appears to be occluded by silicates instead of iron oxides. In association with the segregation of compositions, we can determine that during the oxidative roasting of gold concentrate, encapsulations of gold by iron oxides were inclined to occur in finer size factions and gold encapsulations by silicates were more likely in coarser size factions.

3.2.3. SEM-EDS Analysis

The microstructures and compositions of the coarse and fine size fractions of calcine were further studied by SEM-EDS analysis. The results are shown in Figure 4 and Table 5.

Figure 4a,d shows the SEM image of the coarse particle and the fine particle, respectively. Further partial enlargement (amplification ×10,000) of the marked area in Figure 4a,d is presented in Figure 4b,e, respectively. It is clearly indicated that the surface structure of the coarse particle was relatively compact than the fine particle. Additionally, the EDS spectra of the calcine particles, i.e., Figure 4c,f, and the quantitative EDS analysis (see Table 5) indicate that the coarse particle contained significant quantities of SiO₂ (52.67%) and Al₂O₃ (24.68%). Conversely, the fine particle was mainly composed of iron oxides, i.e., hematite Fe₂O₃ (89.91%).

The results of SEM-EDS are in line with the above analysis, and the porosity of coarse particles was possibly blocked by melted silicates during oxidative roasting to hinder the gold leaching. Meanwhile, it was more likely for fine particles to form the encapsulation of gold by iron oxides.
3.3. Enhancement of Cyanide Gold Leaching from the Different Size Fractions of Calcine

Based on the above analysis related to particle characteristics, the different size fractions of calcine were pretreated by alkali washing, acid picking or sulfuric acid curing-water leaching to expose the locked gold, aiming to enhance gold leaching. The results can be seen clearly in Table 6.

Figure 4. SEM images and EDS spectra of the calcine: (a–c) the coarse particle; (d–f) the fine particle.

Table 5. Results of quantitative EDS analysis of the calcine/(mass fraction, %).

<table>
<thead>
<tr>
<th>Size Fraction/μm</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>SO₃</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>+75</td>
<td>6.14</td>
<td>52.67</td>
<td>26.48</td>
<td>2.77</td>
<td>2.73</td>
<td>1.74</td>
<td>6.53</td>
</tr>
<tr>
<td>−37</td>
<td>89.91</td>
<td>4.85</td>
<td>2.63</td>
<td>0.64</td>
<td>1.41</td>
<td>0.11</td>
<td>0.24</td>
</tr>
</tbody>
</table>
According to the results in Tables 3 and 6, the total gold leaching ratios all presented a significant improvement from the pretreatments with alkali washing, acid pickling and sulfuric acid curing–water leaching, increasing from 70.2% to 84.1%, 80.0% and 89.9%, respectively. Particularly, the alkali washing pretreatment was more effective to expose the gold encapsulated in the coarse and medium size fractions. The gold leaching ratio could grow from about 70%~80% to over 90%. Alkali washing is effective in damaging the silicates structure as reported [30,31], thereby noticeably exposing the gold encapsulated by silicates. With regard to exposing gold locked in iron oxides, an effective dissolution of iron oxides can be achieved by sulfuric acid curing–water leaching attributing to the formation the soluble rhomboclase, whereas only limited dissolutions are attained by acid picking due to the restricted dissolution kinetics of $\alpha$-Fe$_2$O$_3$ formed after the roasting. Thus, comparing with acid pickling, it was more favorable to open the encapsulation of gold in the fine size fraction by sulfuric acid curing-water leaching. The gold leaching ratio could be improved substantially from 59.7% to 95.2%.

In association with the segregation of composition, the above enhancement of gold leaching can be interpreted by the deduction that the pretreatment of sulfuric acid curing-water leaching can effectively dissolve the high content of iron oxides in finer particles while alkali washing can dissolve the high content of silicates in coarser particles.

According to the above studies, we find that the main encapsulation phase of gold varies with the size fraction of calcine. Thus, it is proposed that the relatively coarse size fraction (+37 µm) be pretreated by alkali washing whilst the fine size fraction (−37 µm) is pretreated by sulfuric acid curing–water leaching. Then the two washed residues were evenly mixed and the chemical phase analysis results of gold in the mixed residue are shown in Table 7. It is clear that the distribution of leachable gold in the calcine reached up to 93.84%. Afterwards, the cyanidation of the mixture residue, the gold leaching ratio could increase substantially to 93.6%. The improved process flowsheet of leaching gold from the calcine is recommended as presented in Figure 5. Based on the different predominant encapsulation phase of gold in different size fractions of the calcine, purposeful pretreatments are taken to maximize the exposure degree of gold in this new process, so the extraction of gold from the calcine could be enhanced efficiently.

<table>
<thead>
<tr>
<th>Phase of Gold</th>
<th>Exposed Gold</th>
<th>In Sulfides</th>
<th>In Oxides</th>
<th>In Silicates</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/(g/t)</td>
<td>21.02</td>
<td>0.41</td>
<td>0.82</td>
<td>0.15</td>
<td>22.40</td>
</tr>
<tr>
<td>Distribution/%</td>
<td>93.84</td>
<td>1.82</td>
<td>3.68</td>
<td>0.66</td>
<td>100.00</td>
</tr>
</tbody>
</table>
4. Conclusions

The total gold leaching ratio of a refractory As-, S- and C-bearing gold concentrate calcine by direct cyanidation was only 70.2%, but there was a significant variation in the gold leaching ratio based on size fraction, in the following order: medium size fraction (82.6%) > coarse size fraction (72.3%) > fine size fraction (59.7%). Due to the grindability difference of minerals and the intimate occurrence of Au with S and Fe in the raw gold ore before flotation, segregation of composition occurred—the coarse and medium size fractions always had much higher SiO$_2$ content whilst Fe and Au were prone to being concentrated in finer size fractions. As a result, the encapsulation of gold by iron oxides was apt to occur in finer calcine particles, whilst the gold encapsulation by silicates occurred more easily in coarser particles because the porosity of particles were blocked by melted silicates.

The enhanced gold leaching tests showed that alkali washing was more effective for exposing the gold encapsulated in the coarse and medium size fractions due to effectively damaging the silicates structure and sulfuric acid curing-water leaching was more favorable to open the encapsulation of gold in the fine size fraction attributing to remarkable dissolution of iron oxides via forming the soluble rhomboclase. Hence, via the pretreatments of alkali washing for the relatively coarse size fraction (+37 µm) and sulfuric acid curing-water leaching for the relatively fine size fraction (−37 µm), the total gold leaching ratio of calcine by cyanidation was improved from 70.2% to 93.6%, which is substantial. Based on the composition segregation associated with particle size, this is an efficient way of intensifying gold extraction for this kind of refractory As-, S- and C-bearing gold concentrate calcines.

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

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