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REFRAKTER ALTIN CEVHERLERİ İÇİN TANIMLAYICI ÇÖZÜNDÜRME TEKNİĞİNİN UYGULANMASI

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ÖZET

Bu çalışmada, Kaletaş (Gümüşhane-Türkiye) cevherinin tanımlayıcı liç tekniğiyle refrakterlik davranışı araştırılmıştır. Ayrıca altın kazanımını artırmak için siyanür liçinden önce ultra-ince öğütme de araştırılmıştır. Aşırı öğütülmüş cevherin iki aşamalı siyanür liçi cevherdeki yavaş ve hızlı çözünebilen altının toplam kazanımını %93' e kadar artırmıştır. Tanımlayıcı liç tekniği göstermiştir ki, altın cevher matriksindeki silikatlar, sülfitler, oksitler ve karbonatlar içerisinde çok ince taneli olarak bulunmaktadır.

Anahtar Kelimeler: *Altın Cevherleri; Refrakterlik; DiagnosticLiç*

APPLICATION OF DIAGNOSTIC LEACHING TECHNIQUE FOR REFRACTORY GOLD ORES

ABSTRACT

In this study, the refractory behavior of Kaletaş (Gümüşhane-Turkey) ore was investigated within a diagnostic approach. Ultrafine grinding prior to cyanide leaching was also examined to enhance the gold recoveries. Two-stage cyanidation of ultrafinely ground ore was found to improve the extraction of gold to 93% with the implication of presence of readily recoverable gold and slowly dissolving gold in the ore. Diagnostic leaching provided an insight into the refractoriness of the ore, which could be attributed to the very fine gold particles locked up largely within the carbonates, oxides and sulfides and, to a small extent, within silicates present in the ore matrix.

Key Words: *Gold ores; Refractoriness; Diagnostic leach*

1. INTRODUCTION

Gold ores can be broadly categorized as "free milling" and "refractory" depending on their response to cyanide leaching [1]. A gold recovery of >90% can be readily achieved with a conventional cyanide leaching of free milling ores [2]. However, refractory gold ores are often characterized by the low gold extractions (<50-80%) in cyanide leaching. The refractoriness of gold ores and concentrates stems primarily from the inherent mineralogical features with reference to the mode of presence and association of gold and carbonaceous matter present. In practice, the refractoriness has been reported to be caused by following reasons:

- Very fine dissemination (<10 µm) or presence of gold particles as solid solution within mostly pyrite and arsenopyrite
- Association and presence of gold with tellurides and base metal sulfides of lead, copper and zinc
- Carbonaceous matter and silicate minerals present
- Ultrafine gold locked up in the gangue matrix (mostly quartz) or complexes with manganese oxides.

A suitable pre-treatment process is often required to overcome the refractoriness and render the gold accessible to the lixiviant action of cyanide and oxygen [3]. Ultrafine grinding, modified cyanidation, roasting, pressure oxidation and bacterial oxidation are the pretreatment methods currently practiced for refractory gold ores and concentrates [4,5]. Ultrafine grinding is one method for liberating of locked gold for some ores if efficient size reduction is obtained [6]. Ultrafine grinding followed by cyanide leaching can sometimes produce acceptable recoveries. However, gold in solid solution can only be effectively recovered if the matrix is altered by some chemical or biological pretreatment [7]. Roasting, simple stage process using fluidized bed roaster at around 650^{o}C, is one of the most common method for the treatment of gold-bearing pyrite/arsenopyrite and pyrrhotite concentrates to produce porous calcine and hence to increase the amenability to cyanidation [8]. Dunn and Chamberlain (1997) showed that a gold bearing arsenopyrite concentrates including 70% arsenopyrite and 25% pyrite were pyrolsed at 700^{o}C for 30minutes, and then oxidized for two hours in pure oxygen at 550^{o}C and cyanide leached, the gold recovery increased to 97% [9].

Pressure oxidation and biooxidation methods has gained importance in recent years mainly due to the environmental problems (e.g. SO_2 emissions) associated with roasting process [10]. Lehman et al. (2000) studied the fine grinding, pyrolysis-roast (Pyrox) and an oxidative pressure acid leach (PAL) on gold existed in solid solution in an arsenopyrite matrix. The PAL process produced a slightly better gold recovery of 79% compared to the Pyrox recovery of 75%, and both of these were greater than the 55-60% recoveries achieved with the untreated ore [7]. Gunyanga et al. (1999) studied the roasting and pressure oxidation leach test on a flotation concentrates ground to 50% minus 45 microns with 80 gr/t Au grade. While roasting and cyanidation test results shown gold recovery of 75%, a pressure oxidation process in an autoclave resulted in substantially higher gold recoveries (>90%) over shorter periods [11]. Biooxidation experiments carried out on a refractory Au ore concentrate containing 2.32 % arsenic and 3 1.04 g/t showed that only about 40% of the Au could be recovered from the concentrate by cyanidation without pretreatment and only 46% recovered after roasting and cyanidation, it was possible to recover 76% of the Au after biooxidation and cyanidation [12]. Ubaldini et al. (1999) studied the bioleaching with *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* investigated at a bench scale on a refractory gold-bearing arsenopyrite (2 g/t Au) ore. Gold recovery reached about 55.3% after 48 h of cyanidation with fine grinding to -30 μm of ore. After bench-scale bacterial oxidation experiments under different operating conditions, gold recoveries were higher (>%90) than those obtained from direct cyanidation [13].

Before determination recovery method, as an analytical technique, diagnostic leaching is very useful in establishing the ratio of gold associated with different mineral phases in an ore.

2. DIAGNOSTIC LEACHING

The adoption of a particular pretreatment route is based primarily on the economics of gold recovery. However, the mode of occurrence and association of gold is of practical importance for the nature of refractoriness. Once such information is known that pretreatment strategy can then be developed to manipulate and modulate the process variables to maximize gold recovery in the following cyanidation stage. Diagnostic leaching may be explored to provide an insight into the deportment of gold within ore. Diagnostic leaching involves the selective decomposition of the mineral phases and to extract the gold exposed from the mineral removed in the subsequent cyanide leaching step. A set of guidelines for the design of a diagnostic leaching experiment has been demonstrated by Lorenzen (1995) [14]. Table 1 shows the set of treatments for the likely elimination of mineral phases in a diagnostic leaching method. However, the procedure can be tailored to the mineralogical composition of the ore examined [15].

In the technical literature on the subject, it is generally agreed that gold+silver tellurides dissolve at a slower rate than native gold and electrum. Also, leaching rates can be increased by ultrafine grinding, increasing the pH to 12.0 to 12.5 and use of oxygen rather than air as oxidant. This method known as two-stage cyanidation can be considered to be an example of diagnostic leaching. The basis of this procedure is to leach in dilute cyanide (0.1%) at pH 9.5 for 24 hours to dissolve native gold but not gold+silver tellurides (Stage 1), followed by a strong cyanide (2%) leach at pH 12.5 for 96 hours to dissolve gold+silver tellurides (Stage 2) [16].

Henley et al. (2000) investigated the dissolution of native and gold+silver tellurides in a flotation concentrate with a head grade of approximately 37ppm Au and 47ppm Te in cyanide solution. They have tested a diagnostic leach procedure to quantify Au in native gold and in gold + silver tellurides in which the Au is present in native gold (≅77%), calaverite (≅23%) and Au-bearing hessite and petzite (<1%) [16]. Teague et al. (1998) studied that diagnostic leaching was performed on refractory gold ore containing 5.9% pyrrhotite, 0.9% pyrite, 1.3% arsenopyrite and bulk concentrates generated from the flotation tests. Results showed that significant proportions of gold were locked within refractory pyrrhotite (≅10%) and pyrite (≅20%). The proportion of free gold in the concentrate was approximately ≅70% [17]. Lorenzen and Van Deventer (1993) used diagnostic leaching to identify the refractory nature of gold ores. 1.3% to 2.4% of the gold content was leachable with direct cyanidation. Thus, approximately 95% of Au in ore was extracted by means of selective destruction with nitric acid sulphuric acid of minerals [18].

Table 1. Diagnostic leaching procedure by selective destruction of gold ores [18]

Treatment	Minerals likely to be destroyed
NaCN	Gold
Na_2CO_3	Gypsum and arsenates
HCl	Calcite, Dolomite, Galena, Pyrhotite, Goethite
$HCI/SnCI_2$	Hematite, Calcine, Ferrites
H_2SO_4	Cu-Zn sulphides, Labile pyrite
$FeCI_3$	Sphalerite, Labile Sulphides, Tetrahedrite
HNO_3	Pyrite, Marcasite, Arsenopyrite,
Oxalic Acid Washes	Oxide Coatings Silicates
HF	Silicates
Acetonitrile elution	Gold adsorbed on carbon

Kaletaş gold ore offers an estimated resource of 362 000 tonnes ore with an average grade of 6.8 g/t Au [19]. The Kaletaş disseminated gold occurrence, hosted by thin-bedded, silty to sandy limestones, consists of siliceous lenses developed along permeable zones such as fault, fracture and bedding planes. Gold is enriched in silicified limestones, especially along zones of extensive carbonate removal. The gangue minerals are composed of calcedonic quartz, calcite, dolomite, illite and halloysite [20].

In previous studies [21] in cyanide leaching tests, the gold recovery from Kaletaş ore has been reported to be limited to 50-67 %. Roasting (at 550^{o}C) as a pretreatment step before cyanidation was shown to improve the recovery of gold only to 80 % [22]. Similarly, Celep et al. (2005) noted only a marginal improvement in the gold extraction (70 %) from the roasted ore compared with that from the untreated ore [23]. Also, Gönen et al. showed that while the gold extraction extent obtained under optimum conditions (-0.038 mm particle size, pH=1.5, mixing time = 5 h, 15.2 kg thioures/ton ore, 140.9 kg iron(III) sulfate/ton ore) was 66.73%, gold recovery was 74.94% at experiments performed using the CIL process by adding activated carbon during leaching. The 8% increase in leaching extent is a significant technological improvement for the applicability of CIL (carbon in pulp) process [24]. These studies concluded that Kaletaş ore was refractory in nature though the nature of refractoriness was unclear.

In this study, the application of diagnostic leaching procedure to determine the refractory characteristics of Kaletaş gold ore was investigated. Furthermore, ultrafine grinding as a pretreatment step before two-stage cyanide leaching was examined to determine the gold available to cyanidation and to identify the leachability characteristics of the gold particles present in the ore.

3. MATERIAL AND METHOD

3.1 Material

A total amount of 150 kg ore sample was obtained from Kaletaş (Gümüşhane) gold deposit. A number of hand-picked pieces of the ore were separated for the mineralogical analysis. The polished sections prepared from the hand-picked pieces for mineralogical examination were examined under an ore microscope (Leitz Wetzlar). The remaining bulks of the samples were reduced to -4 mm using jaw and roll crushers, and riffled to obtain 2 kg representative sub-samples. These were then ground (80% passing 38 µm) in a laboratory rod mill for two-stage cyanide leaching of ultrafinely ground ore experiments and diagnostic leaching tests (Figure 1). The chemical composition of the ore sample is presented in Table 2. The ore sample was determined to contain 6.8 g/t Au and 1.2 g/t Ag.

The chemical and mineralogical analysis of the samples used in this study indicated that the ore consisted of predominantly quartz, calcite and, to a less extent, silicates and sulphides of Pb, Fe, Zn, As and Cu. Pyrite, realgar, orpiment, marcasite and native sulphur were identified as sulphide phases. Quartz and calcite were the most abundant non-sulphide phase. Pyrites were commonly present as particles of 3-75 µm in size and as finely disseminated within quartz (Fig. 2). Gold were present as native and electrum form. The occurrence of gold in electrum can lead to slower gold leaching kinetics, and also cyanide consumption can increase from the reaction of oxides or sulphides. Organic matter was also identified to be present in the ore. Preg-robbing behavior may happen from natural carbonaceous materials in the ore that may adsorb gold.

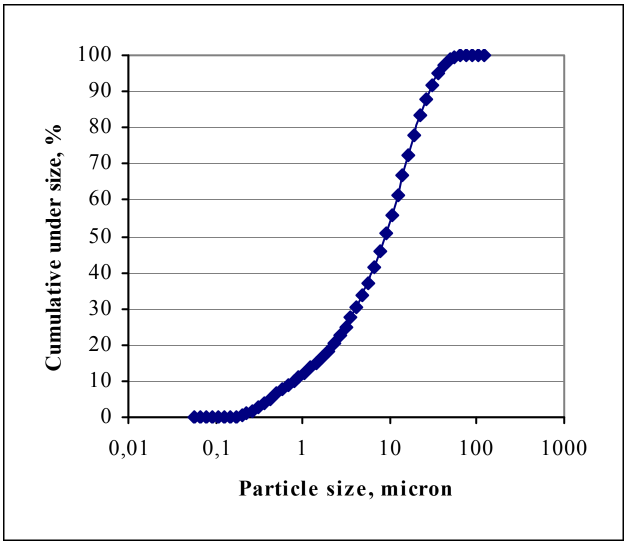

Figure 1. Cumulative particle size distribution of samples used in tests

Table 2. Chemical composition of the ore sample

Compound	Content (%)	Element	Content (ppm)
SiO_2	54.89	Au	6.8
Al_2O_3	4.88	Ag	1.2
Fe_2O_3	2.38	Cu	281.0
CaO	17.86	Zn	242.0
As	3.88	Pb	359.0
MgO	0.30	Sr	223.7
Na_2O	0.09	Sb	101.9
K_2O	0.14	Ni	46.0
TiO_2	0.09	V	42.0
P_2O_5	0.52	Co	16.1
MnO	0.03	Zr	17.9
Cr_2O_3	0.02	U	6.6
LOI	16.30	Cd	2.1
Tot. C	3.75	Ga	3.3
Org. C	0.18		

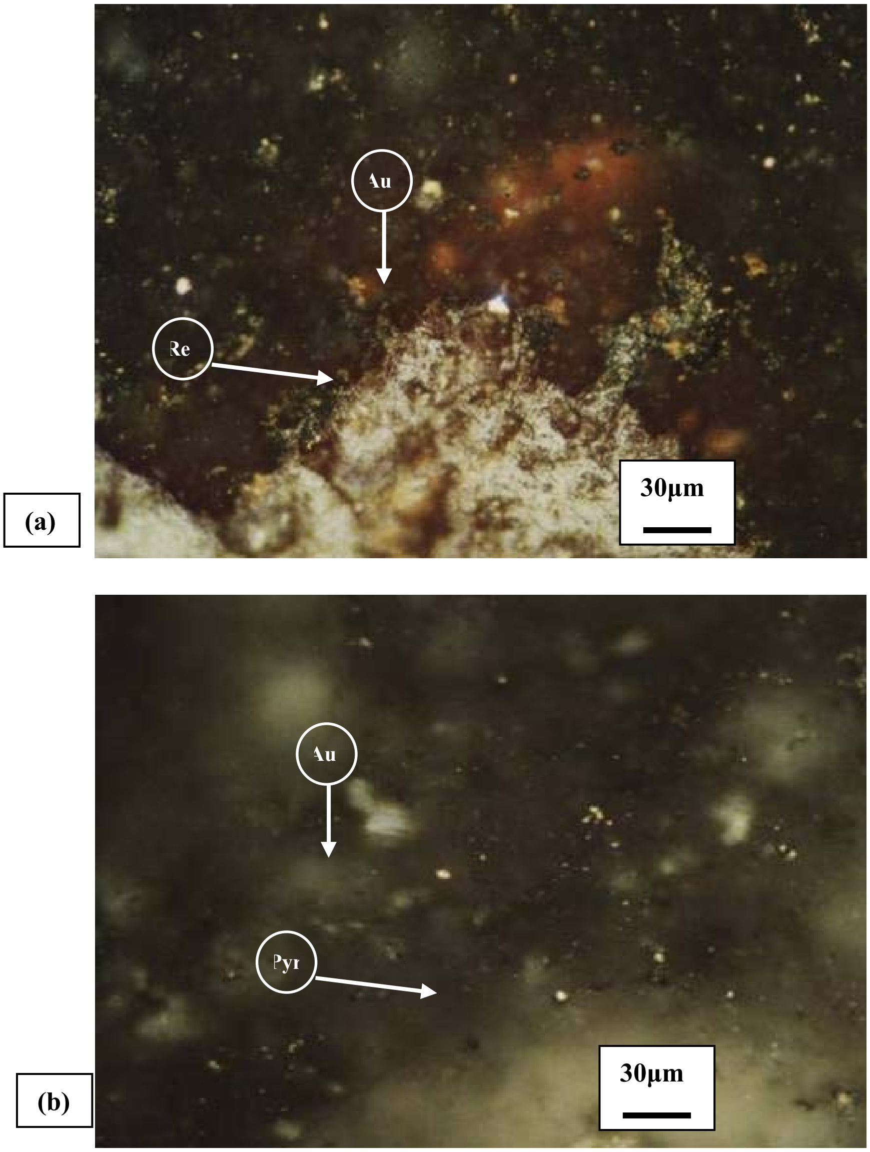

Figure 2. (a) A view of a Au particle (9 µm) as electrum and realgar grain (Re) in quartz matrix and (b) A view of Au (3,5µm) and pyrite (Pyr) grains in quartz matrix

3.2. Method

The cyanide leaching tests (24 h) were performed in a glass reactor (plexiglass reactor for HF leach) equipped with a pitched blade turbine impeller rotating at 1400 rpm (Figure 3). NaCN concentration was maintained at 1.5 g/l over the leaching period and the consumption of cyanide was recorded. Diagnostic leach tests involved a series of acid leaching stages aimed to destroy specific minerals, followed by cyanidation of the residue from each stage. Table 3 shows the sequence and conditions of acid leaching steps in diagnostic leach tests. Conditions for two-stage cyanide leaching of ultrafinely ground ore to determine the gold available to cyanidation are presented in Table 4.

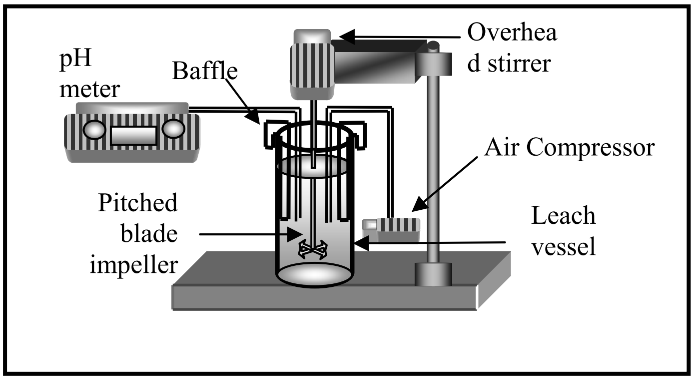

Figure 3. Experimental set-up for diagnostic leaching of the ore

Table 3. Sequence and conditions of diagnostic leaching of the ore sample (80% passing 37 μm) [14, 18].

Treatment Stage	**Leach Parameter**	**Minerals likely to be destroyed**
NaCN, 1.5 g/l	24 h, pH 10.5 (with NaOH)	Gold
HCl (12%)	L/S=2:1, 8 h; 60°C	Calcite, Dolomite, Galena, Pyrhotite, Hematite
H_2SO_4 (48%)	L/S=2:1, 5 h; 80°C	Cu-Zn sulphides, Labile pyrite
HNO_3 (33%)	L/S=2:1, 6h; 60°C	Pyrite, Marcasite Arsenopyrite,
HF (20%)	L/S=2:1, 6h	Silicates
Acetonitrile elution (40%)	L/S=2:1, 6 h; 10 g/l NaCN	Gold adsorbed on carbon

Table 4. Conditions for two-stage cyanidation of ultrafinely ground (6 h) ore [16]

Conditions	**Stage**	**Gold**
NaCN (1.5 g/l) 24h, pH 10.5	Stage I	Native, electrum and metastable gold
NaCN (20 g/l), 96 h, pH 12, 1kg/t $Pb(NO_3)_2$	Stage II	Gold tellurides
Remaining gold	Invisible gold, Au selenide-metalloid-sulfides	

Analysis of gold in the samples removed at predetermined intervals was carried out using an AAS. Leach residues at the end of each stage were also analyzed for gold to establish mass balance and determine the gold recovery. CN^- concentration was determined by titration with silver nitrate using rhodanine as the indicator.

4. RESULTS AND DISCUSSI0NS

4.1. Two-stage cyanide leaching of ultrafinely ground ore

Figure 4 shows the results of two-stage cyanidation after ultrafine milling of the ore. These tests were designed to clarify whether the low gold extraction was due to the incomplete “liberation” of gold particles for cyanidation. The findings indicated that 74% of gold could be recovered in Stage I using standard cyanidation procedure adopted in this study. Compared with the earlier findings only a limited enhancement with ultrafine milling was apparent. In Stage II, the residues from Stage I was subjected to extended cyanide leaching using stronger cyanide solution over 96 h (Table 4). A cumulative extraction of 93% Au was obtained in two-stage process. The gold extraction in Stage I could indicate the readily cyanidable gold content of the ore while the result of Stage II showed the presence of gold with slow dissolution characteristics. The findings also revealed that 7% of the gold present in the ore was inaccessible gold.

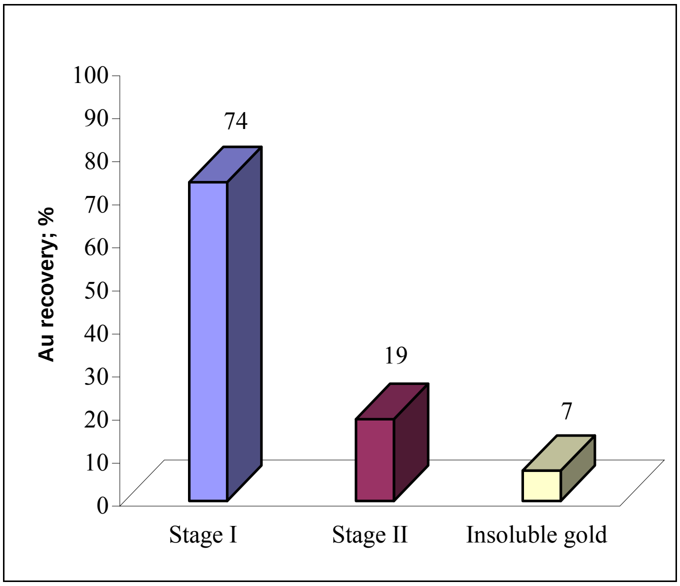

Figure 4. Extraction of gold from the ultrafinely milled (6 h) ore in two-stage cyanidation (parameters in Table 4)

4.2. Diagnostic leaching tests

Figure 5 illustrates the results of the diagnostic leaching of the ore which involves stepwise acid treatment followed by standard cyanide leaching after each stage. Initial cyanide leaching of untreated ore resulted in a gold extraction of 72%, this indicating the cyanide recoverable gold consistent with the findings reported in the previous sections. The remaining portion of the gold appeared to be refractory in character presumably due to the inaccessibility of gold particles to the action of cyanide. A sequence of acid treatment (HCl, H_2SO_4, HNO_3, HF) was shown to improve the extraction of gold to 100%.

It has been reported that sequential acid leaching using HCl, H_2SO_4 and HNO_3 would destroy a variety of mineral phases [18]. It is extremely difficult to quantity the decomposed phases and hence draw firm conclusion from the data due to the non-selective nature of acid treatment expected i.e. partial removal of sulfides by HCl and H_2SO_4 prior to HNO_3 treatment. Notwithstanding this, in the first stage of acid leaching by HCl, the oxides and carbonates would be completely destroyed to expose the gold associated. Further acid treatment with H_2SO_4 and HNO_3 would be expected to remove the sulfides present. It could be estimated from the diagnostic leaching data that the refractoriness of the ore is caused by fine dissemination and association of gold particle within carbonates and oxides (~13%), sulfides (~13%) and silicates (~2%). The results of acetonitrile elution stage suggests that no preg-robbing activity of carbonaceous material present.

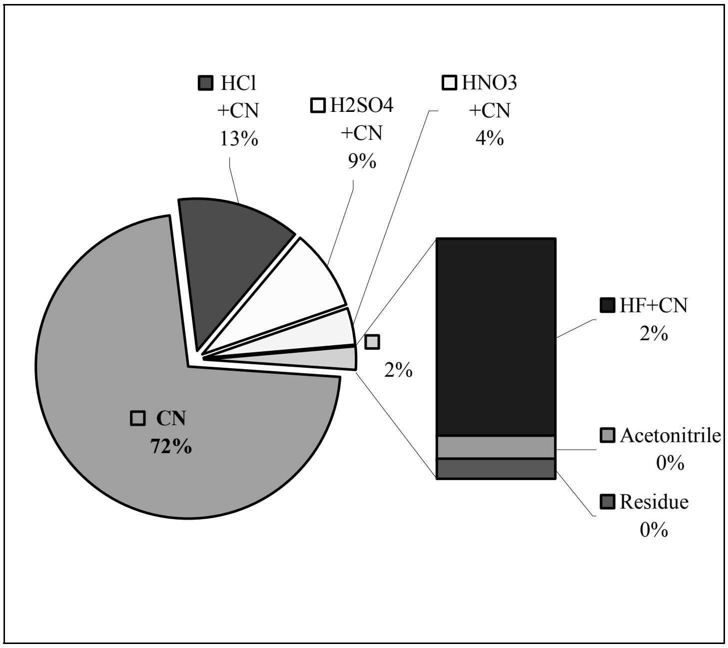

Figure 5. Extraction of gold following each stage of acid treatments with in diagnostic leaching of the ore

5. CONCLUSIONS

In this study, the reasons for the low gold recoveries from the refractoriness of Kaletaş ore were investigated by adopting a diagnostic procedure. Pretreatment of the ore by ultrafine grinding was also examined to overcome the refractoriness and to improve the recovery of gold.

The two-stage cyanidation indicated that 74% of gold was be recovered in Stage I. A cumulative extraction of 93% Au was obtained in two-stage process. The findings also revealed that 7% of the gold present in the ore was inaccessible gold. In the diagnostic leaching tests, it could be estimated from the diagnostic leaching data that the refractoriness of the ore is caused by fine dissemination and association of gold particle within carbonates and oxides (~13%), sulfides (~13%) and silicates (~2%).

The findings of the diagnostic leaching tests and two-stage cyanide leaching of ultrafine milled ore provided invaluable information on the refractory behavior of the ore. It was deduced that the occlusion of very fine gold particles within mineral phases such as carbonates, oxide and sulfides appeared to be the main reason for the refractoriness. Furthermore, the presence of alloyed gold with slow dissolution character could also contribute to the refractory behavior of the ore.

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