

Chapter 8

HYPOCHLORITE LEACHING OF GOLD ORE

by

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ABSTRACT

Cyanide is a conventional lixiviant for gold extraction but its' toxicity is a major concern for the environmentalist. There are many alternative non-cyanide lixivants, such as thiourea, thiosulphate, chlorine and hypochlorite etc., which may reduce environmental sensitivity. This paper will discuss the leaching characteristics of gold in hypochlorite leaching solutions. The dissolution of gold in a hypochlorite solution not only depends on the concentration of the hypochlorite but also on other variables, such as hydrochloric acid, sodium chloride and temperature. The dissolution rate of gold in hypochlorite solution is much faster than other lixivants. Due to the interference of impurities, gold extraction from an ore under ambient conditions requires large quantities of reagents. However, refractory gold ores may be successfully pressure oxidized in an autoclave at reasonably low reagent levels. Gold extraction to the pressure oxidation leach solution is rapid and complete in one stage, thus eliminating the need for further cyanidation.

INTRODUCTION

More than a century ago, gold ores were treated by roasting and subsequent leaching

with aqueous solution of chlorine. Ross (1902) reported that chlorine consumption was 3 - 10 kilograms per tonne of ore and the gold extraction was 90 - 98 per cent. MacArthur and Forrest introduced the cyanidation process in 1887. Cyanide consumption was generally low at 0.5 to 1 kilogram per tonne of ore and resulted in the same relative amount of gold extraction. The more expensive chlorination method was displaced and quickly forgotten. It was suggested by Putnam in 1944 that the chlorination process merited reappraisal. Walker (1956) developed a process at Kalgurgli Ore Treatment Company for the treatment of zinc Merrill slimes by chlorination followed by reprecipitation using sodium sulphite. A similar process was conducted by Finkelstein et al. (1966) in South Africa for the treatment of Merrill slimes and gravity gold concentrates with chlorine leaching. A very high purity gold product at 999.9 parts per thousand was produced.

Schneider et al. (1971) and Guay et al. (1961, 1973) have pre-treated Carlin-type carbonaceous refractory gold ore in Nevada with hypochlorite followed by cyanidation. Gold extraction was improved from 6 - 32 % to more than 90%. The reagent requirement in the pretreatment stage was initially 15 kg of chlorine per tonne of ore and then

increased to 50 kg per tonne. Highly refractory ores might require over 100 kg per tonne to yield more than 83 per cent gold by cyanidation. Sawyer and Hendrix (1988) had investigated the effect of sodium hypochlorite on the gold extraction from a carbonaceous ore in Nevada by heap leaching. Extractions of greater than 70 per cent were attained from three ores. When the hypochlorite pretreatment was followed by cyanidation greater than 85 per cent gold extraction was achieved.

Many investigators, Eisele et al. (1970, 1974), Heinen et al. (1974), Hager and Hill (1970), Landsberg and Hoatson (1970), James and Hager (1978), demonstrated that gold could be extracted from ores by high temperature chlorination, with the products evaporating as auric chloride (Au_2Cl_6) at 200°C to 350°C, as aurous chloride (Au_2Cl_2) at 650°C and forming a vapour phase complex, AuFeCl_6 , at low temperature regime. Palmer et al. (1988) pretreated sulphide minerals by roasting at 500°C - 800°C until oxidation was complete. This was followed by chlorination at 300°C. Gold extraction depended on the source of the samples and ranged from 75% to 98%.

Lichty (1988), Demoupoulos (1989) and Yen (1989) extracted gold from refractory ores by pressure oxidation in a solution containing chlorine, which was produced by decomposing calcium chloride, sodium chloride or hypochlorite in an acidic conditions and elevated temperature. Those processes are simpler and more effective than others and much less environmentally sensitive than conventional processes. This paper will present the leaching characteristics of gold metal and gold ores in hypochlorite solutions containing hydrochloric acid and sodium chloride.

EXPERIMENTAL

Three sources of gold were used in this investigation. An artificial gold precipitate with a grade of 95% Au was supplied by BDH Chemicals Limited, Poole, England.

Tests were conducted using 50 mg of the precipitate per 1000 ml of leach solution.

As well, a free milling and a refractory gold ore were used in this study. The chemical composition of the two ores is shown below:

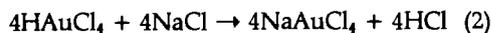
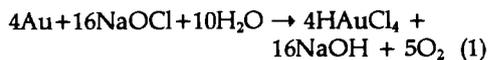
	<u>Free Milling Ore</u>	<u>Refractory Ore</u>
Au (g/t)	9.58	10.5
Ag (g/t)	3.82	98.2
Cu (%)	0.38	0.4
Pb (%)	0.009	1.10
Zn (%)	0.058	0.98
As (%)	0.03	0.45
Fe (%)	6.98	38.10
S (%)	7.00	41.20

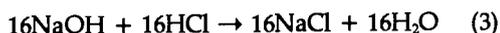
A standard bottle rolls method was used to leach the free milling ore. The leach solution was removed for assay every 2 - 6 hours to a total retention time of 20 - 24 hours. A two litre Parr autoclave was used to treat the refractory ore with the hypochlorite leach solution with 680 kPa oxygen over pressure at 210°C for 90 minutes. After separating the autoclave pregnant solution, the filter cake was washed with a hot 10 % hydrochloric acid solution.

The sodium hypochlorite used in this investigation was in solution form and contained 6 % available chlorine. Calcium hypochlorite was a granular particle containing 50 % available chlorine. All other reagents used were technical grade.

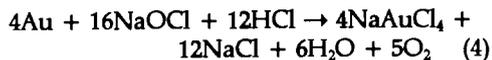
REACTION CHEMISTRY

The reactions between gold and hypochlorite leach solutions containing hydrochloric acid and sodium chloride are demonstrated below:





Overall reaction of equations (1), (2) and (3) can be summarized as follows:



It is obvious that both hydrochloric acid and sodium chloride have affected the gold dissolution in hypochlorite solution.

RESULTS AND DISCUSSION

Gold Precipitate

The dissolution of gold in dilute hypochlorite solution is very slow. With the addition of hydrochloric acid and sodium chloride to the hypochlorite solution, the gold dissolution rate will increase to 20 - 100 mg/cm²/hr, which is 10 - 50 times the rate of gold dissolution in a cyanide solution. Fig. 1

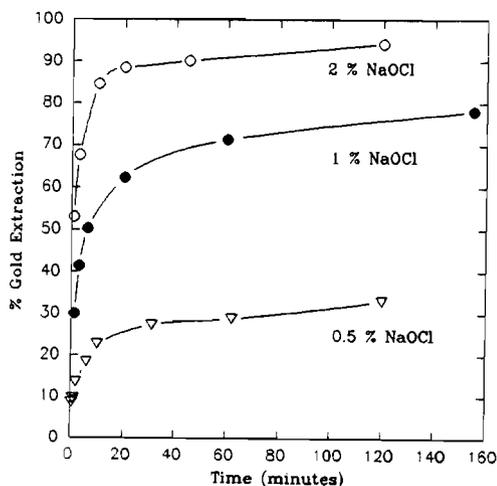


Fig. 1. Effect of Hypochlorite Concentration on Gold Extraction from an Au PPT: 1 % HCl, 1 g/L NaCl

shows the gold dissolution in various solution concentrations of sodium hypochlorite containing 1 % hydrochloric acid and 1 g/L sodium chloride. The rate of gold dissolution is fast initially and then slows down after about 30 minutes. In a

0.5 % sodium hypochlorite solution, less than 30 % of gold is dissolved in one hour. As the concentration of sodium hypochlorite increases the rate of gold dissolution increases. In a 2 % sodium hypochlorite solution, 88 % of the gold is dissolved in 20 minutes and more than 91 % of the gold dissolved in one hour. If the concentration of hydrochloric acid and sodium chloride is increased in the hypochlorite solution, the rate of gold dissolution will further increase. With 5 % HCl and 2 g/L NaCl, 55 % of the gold is dissolved in a 0.5 % NaOCl solution in one hour and 95 % of the gold dissolved in a 2 % NaOCl solution in 30 minutes.

Fig. 2 shows the effect of hydrochloric acid concentration on gold extraction from the gold precipitate sample. The concentration of sodium hypochlorite and

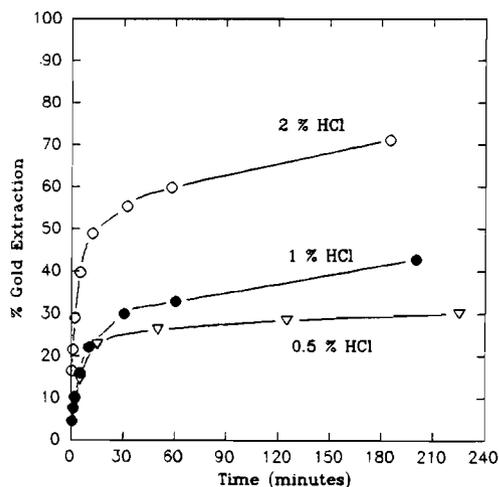


Fig. 2. Effect of HCl Concentration on Gold Extraction from an AuPPT: 0.5 % NaOCl; 2 g/L NaCl

sodium chloride was maintained at 0.5 % and 2 g/L respectively while the hydrochloric acid level varied. In a 0.5 % hydrochloric acid solution, 28 % of the gold was extracted in one hour. Gold extraction increased to 33 % in a 1 % HCl solution and to 60 % in a 2 % HCl solution in the same 1 hour span. Hiskey and Atluri (1988) reviewed an Eh-pH diagram for the Au-Cl-H₂O system, which indicated that the AuCl₄ complex is the only

species stable in the region of pH below 2. The amount of hydrochloric acid required to maintain a pH below 2 depends upon the concentration of hypochlorite in solution. Equation (1) shows that sodium hydroxide is produced when gold is reacted with sodium hypochlorite. Hydrochloric acid is required to neutralize the hydroxide and maintain the pH below 2.

Chloride ions also play an important role in gold dissolution in the hypochlorite solution. Fig. 3 shows the effect of sodium

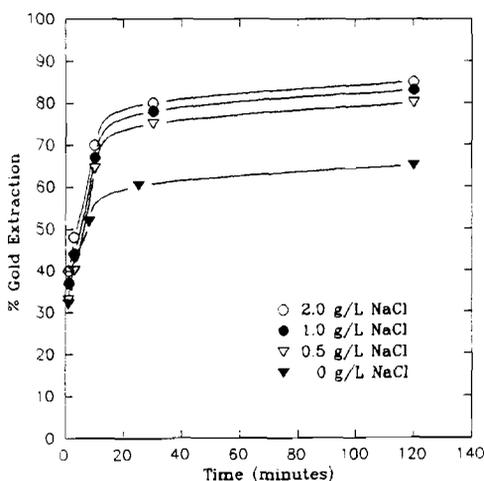
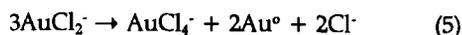


Fig. 3. Effect of NaCl Concentration on Gold Extraction from an Au PPT: 5 % HCl; 1 % NaOCl

chloride concentration on gold extraction from the gold precipitate sample. Without any sodium chloride, 62 % of the gold will be extracted in a solution containing 1 % sodium hypochlorite and 5 % hydrochloric acid in one hour. If 0.5 - 2.0 g/L of sodium chloride is present in the same solution, 80 % of the gold will be extracted under the same conditions. The gold extraction rate is initially very rapid. After 30 minutes a plateau is reached and extended time beyond this results in only a minimal increase in gold extraction. Increasing the concentration of sodium chloride further did not improve conditions for gold dissolution but rather resulted in a decrease in gold extraction. Equation (2) shows that sodium chloride is produced by the neutralization of

sodium hydroxide and hydrochloric acid. High concentrations of sodium chloride may reverse the reaction equation (4). Hiskey and Atluri (1988) explained that the existence of AuCl_2^- in an aqueous solution containing 10^{-2} M Cl^- is not possible as suggested by the disproportionate equilibrium:



By increasing the concentration to about 0.1 M Cl^- , the chloride activity becomes sufficient enough to stabilize the AuCl_2^- complex. Again, the acidity is shown to be important in maintaining the dissolved gold in solution.

All of the above tests were conducted at 22°C. As solution temperature increases, the gold dissolution rate also increases within limit. Fig. 4 shows the effect of temperature on gold extraction from the gold precipitate dissolved in a solution containing 0.5 % NaOCl, 5 % HCl and 1 g/L NaCl. 82 % of the gold was extracted in one hour at 27°C, 92 % at 43°C and 97 % at 55°C. Further increasing the solution temperature to 70°C or higher resulted in decreased gold extraction. This may be due to the greatly decreased chlorine dissolubility in water at higher temperature.

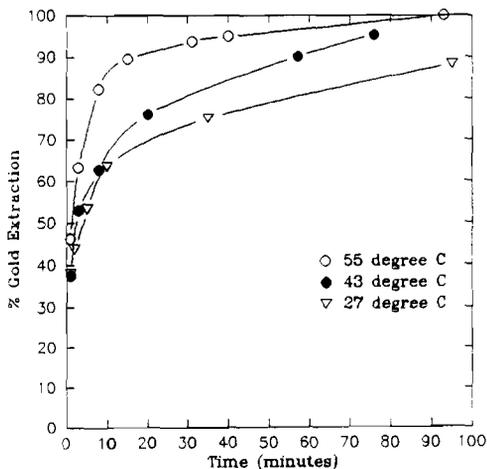


Fig. 4. Effect of Temperature on Gold Extraction from an Au PPT: 0.5 % NaOCl; 5% HCl; 1 g/L NaCl

Free Milling Gold Ore

The free milling gold ore used in this study contains sulphide minerals, such as chalcopyrite and pyrite. Conventional cyanidation resulted in 95 % of the gold being extracted under strong leaching conditions, i.e., a grind of 90 % minus 200 mesh, leach with 1 g/L NaCN at pH 11.0 for 24 hours. The reagent consumptions are 2 kg/t NaCN and 1.8 kg/t CaO. The hypochlorite solution tests reported in this paper were performed on a standard bottle roll machine. In each case, 250 grams of sample was slurried with 500 ml of the appropriate hypochlorite solution. Initially, the optimum leaching conditions for the gold precipitate (2 % NaOCl, 1 % HCl and 1 g/L NaCl) was used to leach the ore sample. Gold extraction from the ore was very poor because the hypochlorite and hydrochloric acid were consumed by sulphide and gangue minerals. Thus, higher reagent concentrations are required for the ore sample.

Fig. 5 shows the effect of sodium hypochlorite concentration on gold extraction from a free milling ore. The concentration of 20 % hydrochloric acid and 20 g/L sodium chloride was maintained for each test. When the ore was leached with 9

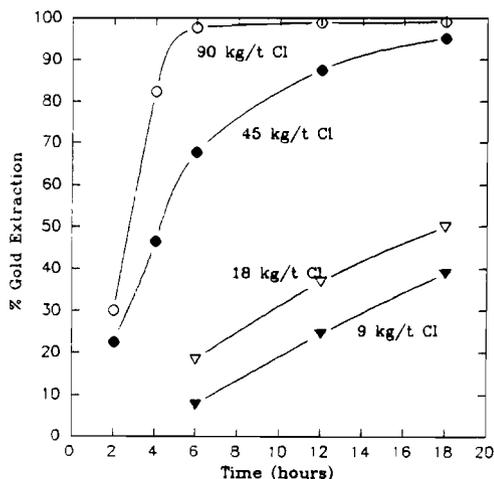


Fig. 5. Effect of NaOCl Concentration on Gold Extraction from An Ore Sample: 20 % HCl; 20 g/L NaCl

kg/t and 18 kg/t of available chlorine, which is equivalent to 7.5 % and 15 % sodium hypochlorite solution respectively (6 % available chlorine), the gold extraction was less than 50 % for the retention time of 18 hours. Using 45 kg/t available chlorine, 95 % of the gold was extracted in 18 hours. If the available chlorine was doubled up to 90 kg/t, 98 % of gold was extracted in 6 hours.

Fig. 6 shows the effect of hydrochloric acid concentration on gold extraction from the ore sample. Other reagent concentrations were 45 kg/t of sodium hypochlorite and 20 g/L sodium chloride. When the hydrochloric acid concentration was reduced by one half to 10 % HCl, the gold extraction was reduced about 10 %, i.e., 86 % gold extraction at 18 hours retention time. A further reduction of the hydrochloric acid concentration to 5 % HCl resulted in gold extraction of less than 70 %.

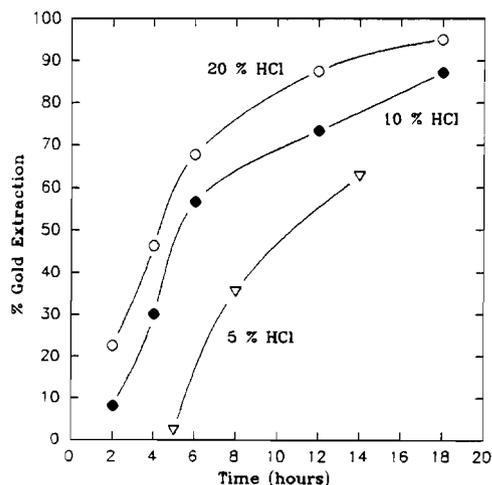


Fig. 6. Effect of HCl Concentration on Gold Extraction from An Ore Sample: 45 kg/t NaOCl; 20 g/L NaCl

The effect of sodium chloride concentration on gold extraction from an ore is shown in Fig. 7. In a solution containing 80 kg/t sodium hypochlorite and 20 % hydrochloric acid, 80 % of the gold was extracted from the ore in 24 hours retention time without any addition of sodium chloride. About 97 % of the gold was

extracted under the same conditions by adding some sodium chloride, either 20 kg/t or 40 kg/t.

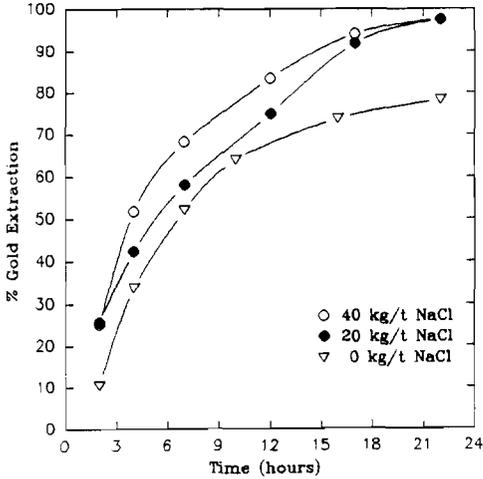


Fig. 7. Effect of NaCl Concentration on Gold Extraction from An Ore Sample: 80 kg/t NaOCl; 20 % HCl

Refractory Gold Ore

The refractory gold ore used in this investigation is a flotation concentrate containing complex sulphide minerals, such as chalcopyrite, galena, sphalerite and pyrite. Only 10 % of the gold could be extracted by conventional cyanidation. When the ore was pretreated by pressure oxidation followed by neutralization and cyanidation, 95 % of the gold was extracted. Two drawbacks of this process are: (1) very large quantities of lime are required for neutralization and pulp density is difficult to control; (2) silver extraction is very low. Even the hot lime conditioning method could not make much improvement on the silver extraction.

Yen and Pindred (1989) had added sodium hypochlorite to the autoclave during the pressure oxidation of the ore. In a solution containing 120 kg/t chlorine, 98 % of the gold and 87 % of the silver were extracted in one stage. In order to reduce the amount of sodium hypochlorite required, 3 % HCl and 10 g/L NaCl were added in a

24 kg/t available chlorine solution. This resulted in 93 % gold and silver extraction in one stage oxidation.

In this study, sodium hypochlorite was replaced by calcium hypochlorite and the reagent requirement was greatly reduced. Fig. 8 shows the effect of calcium hypochlorite on gold extraction from a refractory ore. A 250 grams sample was slurred with 1000 ml of leach solution containing 3 % HCl and 2 kg/t NaCl. Calcium hypochlorite was added and pressure oxidation was carried out at 210°C for 90 minutes. After liquid and solid separation, the filter cake was washed with a hot 10 % HCl solution. Results indicated that 92 % of the gold and 98 % of the silver were extracted with 5 kg/t Ca(OCl)₂ or 2.5 kg/t of available chlorine. Also, 95 % of the gold and 99 % of the silver were extracted with 10 kg/t Ca(OCl)₂ or 5 kg/t of available chlorine.

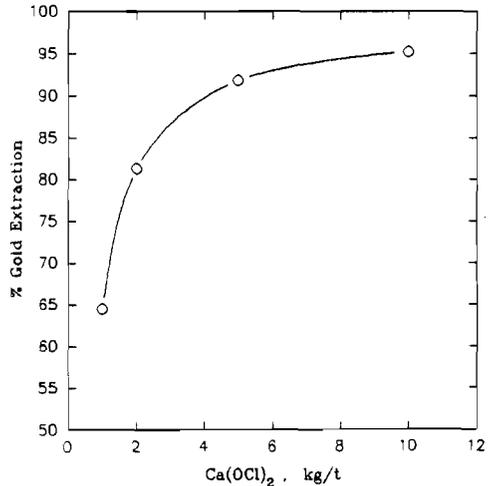


Fig. 8. Effect of Calcium Hypochlorite on Gold Extraction from a Refractory Ore: 3 % HCl; 2 Kg/t NaCl

Fig. 9 shows the effect of hydrochloric acid concentration on gold extraction from a refractory ore in a leaching solution containing 2 kg/t Ca(OCl)₂ and 2 kg/t NaCl. Without any addition of hydrochloric acid, only 37 % of the gold was extracted. Gold extraction was increased with increasing

hydrochloric acid concentration. 82 % of the gold was extracted with 3 % HCl. Silver extraction under those conditions was mediocre but can be improved by further extraction with HCl/NaCl solution. About 98% - 99 % overall silver extraction was achieved by leaching the autoclave residue with 10 g/L NaCl and 10 % HCl solution at 80°C for one hour. The effect of sodium chloride on gold extraction under these conditions was not distinguished and is not described in detail here.

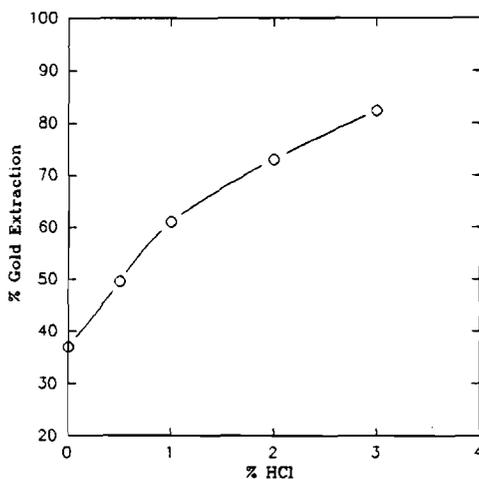


Fig. 9. Effect of HCl Concentration on Gold Extraction from a Refractory Ore: 2 kg/t $\text{Ca}(\text{OCl})_2$; 2 kg/t NaCl

CONCLUSION

Leaching pure gold with an acidic sodium hypochlorite solution has been demonstrated to be effective. The initial rate of gold dissolution was extremely rapid. In a leaching solution containing 1 g/L NaCl, 1 % HCl and 2 % NaOCl, nearly 90 % of the gold was extracted in only 30 minutes. Additions of hydrochloric acid will reduce the sodium hypochlorite requirement. A leach solution containing 1 g/L NaCl, 5 % HCl and 1 % NaOCl achieved nearly the same per cent gold extraction under the same conditions. Raising the leach solution temperature to about 55°C will also enhance the gold dissolution.

Extracting gold from an ore required more reagents and longer retention time because sulphide and gangue minerals consumed sodium hypochlorite and hydrochloric acid. In a leach solution containing 20 % HCl and 20 g/L NaCl, 97 % of the gold was extracted in 6 hours with 90 kg/t available chlorine and 95 % of the gold was extracted in 18 hours with 45 kg/t available chlorine.

For a refractory ore, pretreatment is required in order to expose the gold surface to the leach solution. An acidic hypochlorite solution can be added to the autoclave for pressure oxidation and extraction of the gold at the same time. It required 50 % sodium hypochlorite or 120 kg/t available chlorine to extract 97 % of the gold from the ore. When 3 % HCl and 10 g/L NaCl was added to the leach solution, the same amount of gold could be extracted with 24 kg/t available chlorine under the same conditions. However, the reagent requirement may be further reduced by replacing sodium hypochlorite with calcium hypochlorite. In a leach solution containing 10 kg/t $\text{Ca}(\text{OCl})_2$ or 5 kg/t available chlorine, 3 % HCl and 2 kg/t NaCl, 95 % of the gold was extracted in 90 minutes oxidation at 210°C. Silver extraction was 98 % under the same conditions. This silver extraction can not be achieved by conventional pressure oxidation and cyanidation.

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