IN SITU EXTRACTION OF PRECIOUS METALS AND MINE REMEDIATION WITH POLYSULFIDES

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ABSTRACT

It is estimated that cleanup of metal bearing wastes from abandoned mine lands across the U.S. alone will cost tens of billions of dollars. Recovery of valuable metals by reprocessing of mining wastes in conjunction with water treatment has been considered but hindered by the potential risk of incurring liability in the commercial remediation of abandoned mine sites. Recent US EPA interest in this idea has heightened in the aftermath of the Gold King mine spill because of the potential for mine reclamation that pays for itself by secondary recovery of metal values. At one Superfund site in the southeastern US a pilot test is being developed to test polysulfides for recovery of precious metals while remediating mobile metal contaminants in mining wastes and mine influenced water. Polysulfides are unique in that they have been used to both recover precious metals from ores and for in situ reduction and chemical stabilization of metals during remediation of contaminated sites. In situ treatment of mine pool waters and mine wastes is becoming more common to avoid perpetual water treatment. Polysulfides could be used for in situ recovery (ISR) by stope leaching, for example, while reducing acid generation and metal leaching from abandoned underground mines.

Polysulfides are generally recognized as safe, non-toxic, non-polluting and are routinely used in agricultural applications as well as remediation. Furthermore, polysulfides can be inexpensively produced from ARD and mining wastes themselves. The sulfur saturated system is self-buffering and maintains the optimal chemical environment for leaching precious metals and stabilization of metals such as mercury and base metals. Solvent extraction technology has also been developed to recover gold from polysulfide solutions while recycling and conserving water for sustainable use in metal remediation and recovery.

Demonstrated recovery of precious metals from mined lands using acceptable lixiviants and methods and possibly a first step towards the wider application of ISR for precious metals in undeveloped ores. This paper also touches upon some of the concepts that may lead to the expansion of successful in situ recovery projects.

Keywords: In situ, precious metals, polysulfides, mine remediation

INTRODUCTION

Cyanide has been the reagent of choice to recover gold and other precious metals through leaching since the system was patented the system in the late 1800's[1]. However, it is generally accepted that cyanide would not be allowed for in situ recovery (ISR) of precious metals in most jurisdictions and gaining social license to operate would be very difficult [2]. Hence, there has been considerable interest in developing alternative lixiviants for ISR[3][4]. In the early 1990s the US Bureau of Mines investigated several alternatives to cyanide. One of these technologies involves leaching gold with a polysulfide lixiviant at moderately elevated temperatures where polysulfides are more stable than at ambient temperatures[3][5][6].

The polysulfide lixiviant can be deployed as a dilute, non-toxic, aqueous, solution which operates optimally at neutral pH and elevated temperatures (75 to 150 degrees Celsius (^{o}C)[5]. Polysulfides are still effective at ambient conditions but the solution is not stable and precipitates sulfur[3]. However, the cost of heating solutions and ore would not be prohibitive for some deposits if leach solutions are managed to retain heat in an ISR system[5]. Furthermore, deep deposits naturally attain such conditions and polysulfide compounds injected into these deposits could help stimulate natural dissolution processes and enhance precious metals recovery. It is probable that polysulfide lixiviants can be inexpensively produced from readily available chemical reagents and even mining wastes which has been demonstrated for sulfide leaching[7]. The polysulfide lixiviant is self-buffering and maintains the optimal chemical environment for leaching without extensive operator maintenance[5]. Yet long term rinsing and site monitoring are not necessary because the lixiviant itself is not toxic and breaks down as the system cools and equilibrates after mine closure.

Polysulfide lixiviant systems are promising for ISR of gold and some of the disadvantages of polysulfide leaching by heaps and vat leaching like off gassing and decomposition[3] are less detrimental in ISR systems. However, obtaining permits and social license to operate has always been a “tough sell” for any ISR project[2] owing to public skepticism and concerns over groundwater protection in particular. However, in situ remediation has become a best available technology for groundwater restoration and polysulfides are effective for in situ chemical reduction (ISCR) of metals and inorganic contaminants[8]. Given that abandoned gold mines are often the source of mine influenced water, the author proposes that it may be possible to use ISR and ISCR in tandem to recover gold and reclamation costs for cleanup of these sites while stabilizing metals and reducing treatment costs and longevity. The U.S. Environmental Protection Agency is interested in the potential for mineral and cost recovery at its cleanup sites and has approved a pilot study at the Barite Hill Superfund site in the southeastern US. ISR is not the primary method that will be used at this former heap leach facility but polysulfide recovery of gold from abandoned underground gold mines is a logical extension of the concept. At these sites gold can be recovered from gob and tunnel collapse materials using stope leaching. Furthermore flooding can be used to evoke ISR from tunnel walls and extensions of vein systems where leachable gold occurs in permeable vugs and fractures[9].

Conceptually, ISR and ISCR can be used simultaneously to recover gold and stabilize mine waste and exposed wall rock. The current progress, technical challenges, economics and permitting issues will be outlined in the remainder of the paper.

RESEARCH AND DEVELOPMENT

Leaching Experiments

Ammonia polysulfides have been used for gold leaching and has a fast leaching rate and high leaching ratio of gold in alkaline solutions[3]. It is effective in treating low-grade gold ores and As- and Sb-containing refractory ores. The US Bureau of Mines and University of Minnesota conducted laboratory experiments that showed that polysulfides (S_nS^{-2} where n = 1 to 7) complex with and dissolve gold in sulfur saturated solutions under intermediate H_2S and O_2 partial pressures and neutral pH (Figure 1) according to the following mass balance equation:

$$2Au + H_2S + nS_2 = 2AuS_nS^- + 2H^+$$

The association constants (log K) for aurous polysulfide complexes are between 21 and 26 at temperatures of 100 to 150 ^{o}C. Furthermore, because gold simultaneously forms strong complexes with multiple polysulfides polymers and bisulfide in solution the cumulative association constant is higher than cyanide.

Laboratory tests on pure gold and gold quartz mixtures conducted at 75 to 150 °C and 10 to 100 bars showed the solubility of gold in the presence of polysulfides in of 10 to 50 ppm with a solution containing approximately 500 to 1,600 ppm total dissolved sulfur[6]. Gold solubility is higher with increasing temperature and sulfur concentrations. Extrapolation of these results indicate that gold loadings of 5 ppm can be achieved with a sulfur concentration in solution that is below the equivalent EPA sulfate aesthetic standard of 500 mg/L. Polysulfides ultimately break down into sulfate in relatively oxidizing groundwater conditions.

In another set of experiments some common ore types were "salted" with gold to test the stability of polysulfide in the presence of gangue minerals[10]. The ore samples were collected from the Round Mountain (oxide ore, Nevada), Bullfrog (carbonate hosted, Nevada), and Summitville mines (sulfide ore, Colorado). Because the samples were grab samples and may not be representative of the average ore owing to the "nugget effect", the samples were reacted in a gold pressure vessel to ensure that maximum solubilities could be determined. Rock samples were powdered in a ball mill to <325 mesh grain size in order to accelerate fluid/mineral reactions and to allow more rapid identification of the key processes affecting the integrity of the leach solutions.

The ore samples were reacted with bisulfide and polysulfide bearing solutions at 100-125°C and 100 bars pressures using the autoclave facilities at the University of Minnesota, Department of Geology. Reactants were loaded into a cell (70 ml total volume with a fluid to rock ratio of 3:1 to 10:1) composed of Au and Ti which is itself loaded into an autoclave. The entire autoclave is loaded into a furnace assembly. Fluid samples were periodically withdrawn from the cell so that changes in solution chemistry could be monitored. Fluids were also injected into the reaction cells midway during some of the experiments in order to replace solution removed by sampling and/or to facilitate a needed change in solution chemistry. Experiments involved the injection of relatively simple NaHS solutions(1000 to 1500 mg/l) and if needed a dilute (0.1 M) HCl solution which lowered the pH to the region of polysulfide stability. Solutions were monitored for a large suite of elements including major elements, sulfide sulfur, total sulfur, sulfate, pH (25°C) and dissolved metals (Au, Fe, Cu, Zn) in addition to many other elements.

The maximum and minimum measured gold concentrations during these experiments are tabulated in Table 1. All reported concentrations are economically viable by comparison with typical gold concentrations in standard heap and vat leaching systems. The Round Mountain and Bullfrog ore types required acid and bisulfide additions to achieve optimal gold concentration owing to sulfide oxidation by hematite and dissolution of carbonate. The Summitville samples had natural native sulfur which buffered the solution chemistry at optimal leaching conditions which are approximately neutral as shown in Figure 1 as compared to the alkaline conditions needed for other alternative lixiviants. The fact that this assemblage contained elemental sulfur suggested that to produce polysulfide solutions all that was necessary was to inject NaHS solution. Production of polysulfides by reaction with elemental sulfur would then occur naturally via a process such as:

$nS + HS^{-} = S_nS^{-2} + H^{+}$.

When NaHS solutions were reacted with this ore specimen, the gold concentrations to be quite high throughout the experiment: up to 18 ppm at 125°C and approximately 8 ppm later in the experiment when temperature was reduced to 100°C. Sulfur can also be readily introduced into an ore by precipitation from supersaturated solutions and will likely result in ISR operations involving polysulfide leaching. While too much sulfur can clog pore space the material can be redissolved by adjusting the injection solution as was the case for the Summitville experiment. Hence chemical buffering at optimal pH and Eh conditions (Figure 1) is achieved readily.

Chemical Stability

One drawback of polysulfides is that they are inherently stable and more effective at dissolving gold under elevated temperature conditions (≥75°C) than typical ambient temperatures[3][6]. However, other lixiviants for precious metals also have stability problems. Polysulfides are potentially more stable than other lixiviants in situ because confining pressures and elevated temperatures can be maintained more readily. ISR usually involves saturated conditions which prevent gas exsolution and polysulfide decomposition if hydraulic pressure is high enough. The modest temperatures required to make polysulfides more effective can be attained cost effectively owing to the insulating properties of rock once heated.

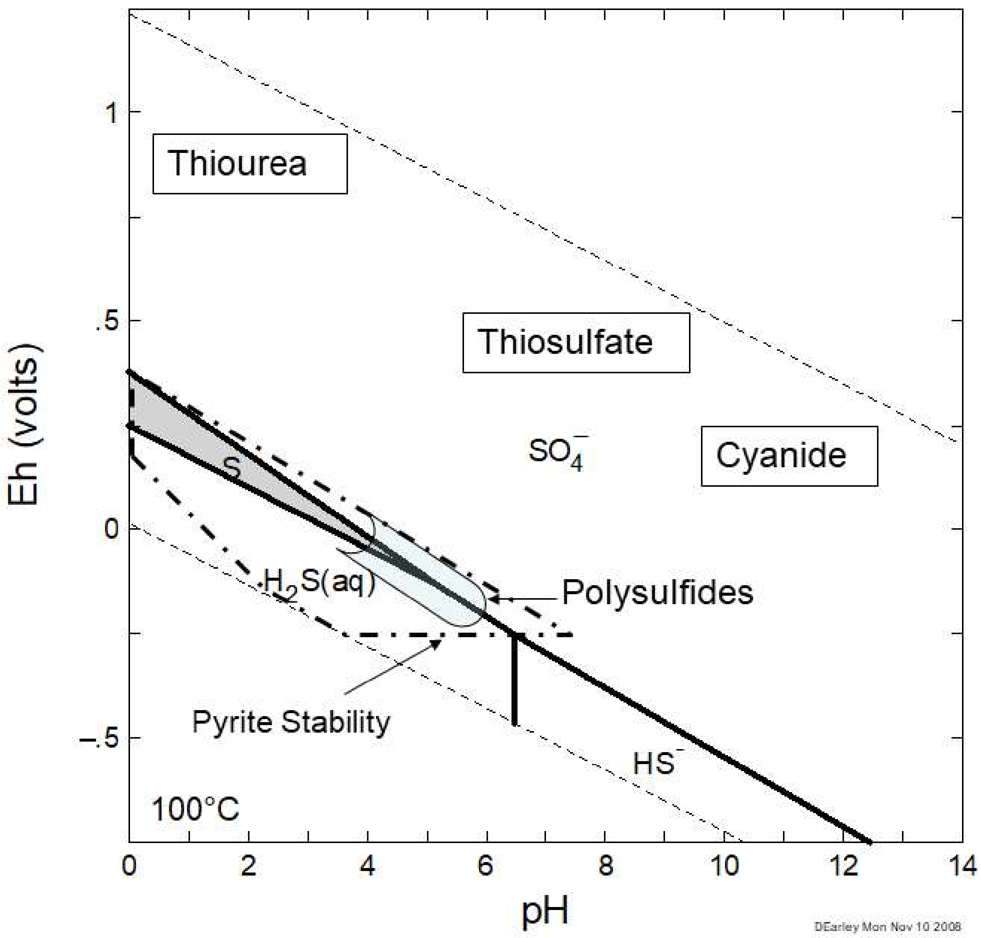

Figure 1: Eh pH Diagram for Sulphur and Polysulfide Aqueous Complexes

IN SITU RECOVERY

Wellfield and Underground Leaching

Traditional wellfield injection and recovery systems can apply to gold and other precious metals for specific disseminated ore deposit types such as placer and Carlin Type ores with sufficient permeability. However alternative gold leaching systems involving bonanza type veins could also be candidates for ISR. At the Ajax underground mine in Colorado, USA an ISR test was conducted with a chloride plus iodine solution injected into a gold-bearing vein(10) The solution was injected at the top of the vein and allowed to flow under gravity to drifts where they could be collected. Solution losses and metallurgical complications resulted in poor recovery and test termination. However, it may be possible to conduct a similar test with polysulfides a more favourable deposit and using better solution tracking and control technology. Certainly the potential for stope leaching in inactive or abandoned underground mines is promising.

So far there have been few studies of the hydraulic properties of gold ores for ISR. The results of porosity and permeability testing of representative samples from the Phoenix Mine in Colorado, USA are provided in Table 2. The hanging and footwall rocks show very low permeabilities that are for the most part lower than the detection limit of the method. However, the vein sample, which hosts most of the gold mineralization, shows the highest permeability which agrees with the observed friability of the vein material. This friability may be a result of fault motions along the plane of the vein(11). Conversely the low permeability of the vein walls ensures solution containment.

Table 1: Polysulfide Leach Test Results

Sample Source	Ore Type	Gold Concentration (mg/L)	
		Maximum	Minimum
Round Mountain Mine, Nevada USA	Oxide	16.8	0.22
Bullfrog Mine, Nevada USA	Carbonate	6.6	3.3
Summitville Mine, Colorado USA	Sulfide	17.9	8.4

Gold Recovery and Processing

Recovery of gold from high temperature solutions can be achieved by simple closed system boiling[5]. Familiar solvent extraction of gold from leach solutions is also possible[12]. Potentially solution grades may be diminished ("preg-robbed) from equilibrium values by co-precipitation of gold with metal sulfides if ISCR results in precipitation of contaminant metal sulfides.

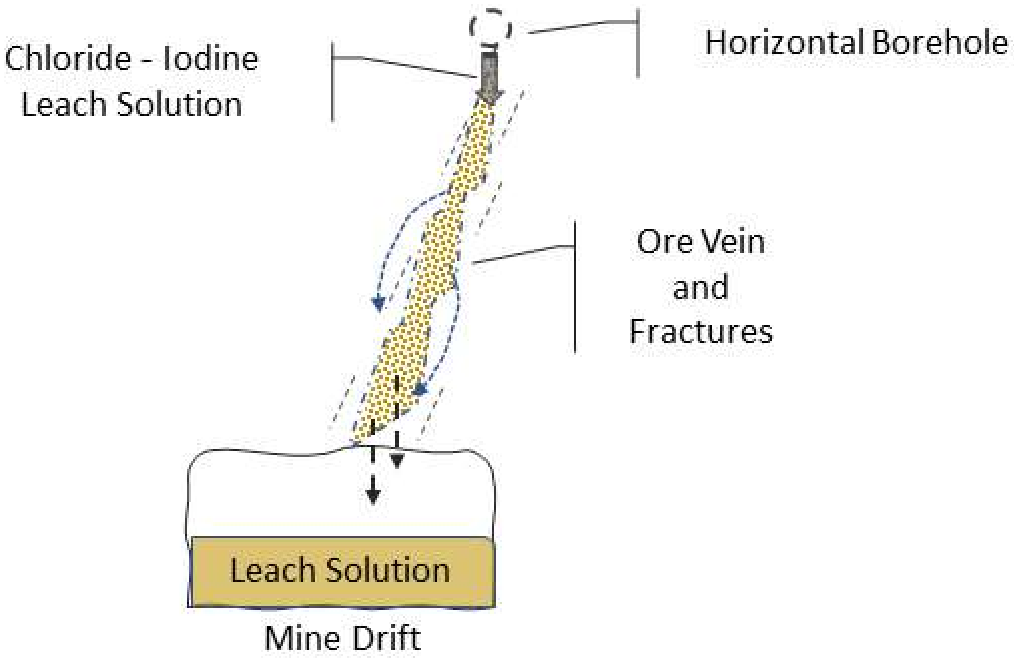

Figure 2: Ajax Mine, Colorado, USA, ISR Test Schematic[10]

Table 2: Hydraulic Properties of the Phoenix Mine Ore and Host Rock, Colorado USA

Sample	Porosity	Permeability	Lithology
	volume %	md	
PH5-1	6.16	2.95E-01	pyrite+quartz vein
PH7-3	6.15	nd	bostonite
PH7-2	7.74	nd	bostonite
PH8-1	8.43	nd	bostonite
PH4-1	6.74	nd	gneiss
PH2-1	3.57	nd	gneiss
PH4-3	7.40	4.86E-01	pegmatite
PH3-2	5.21	nd	pegmatite
md=millidarcy			
nd=not detected			

IN SITU REMEDIATION AND ECONOMICS

In the past few decades in situ remediation has been developed and used extensively for the treatment of organic and metal contaminants. Polysulfide is one of the chemical reagents used for in situ chemical reduction (ISCR) and is recommended by the US Environmental Protection Agency[8]. Polysulfides can passivate chrome, mercury and many metals by ISCR and can even treat cyanide in wastewater[13]. Moreover, injection of ISCR chemicals into a contaminated site is much easier to permit than injection into uncontaminated aquifer under Underground Injection Control and other regulations in the US. Given that there are tens of thousands of abandoned mines across the US alone many sites are likely to be amenable to ISR and ISCR under cleanup actions. These sites have been developed by mining which provides access and enhanced permeability for ISR. Given that these sites are already developed, characterized, and need restoration regardless of metal recovery potential the capital and regulatory risk of attempting ISR at these brownfield projects is considerably lower than for an undeveloped deposit. However, the risk of being involved in responsible party cost recoveries for cleanup may discourage mining companies and other interested parties from the project creating a “Catch 22”.

CONCLUSIONS

Several alternative lixiviant systems for precious metals have been developed and researched thoroughly, but none have contributed significantly to production or facilitated ISR. New mine project investment instruments and regulations lack the flexibility necessary to allow for innovative technology. Hence, the mining industry has not readily embraced alternative leaching technologies such as polysulfides and other alternatives to cyanide for conventional systems much less ISR. Even mature technologies such as thiosulfate and other alternative leaching systems that have been under development for several decades[3] have not yet been been used for ISR. However, the incentives for development of sustainable mining technologies has never been higher. An ISR project based on a leaching system such as polysulfides, which is thought to be a natural agent for mobilizing gold in nature[6], is more likely to gain social license to operate than systems that require artificial chemicals. Indeed, polysulfide solutions could conceivably be derived from mining wastes thereby incorporating the principal of recycling. Moreover, polysulfides can also be used to stabilize and treat mine wastes in situ while potentially recovering metals of value. Mine reclamation cost recovery and water protection could help ISR gain favor and allow ISR to expand to yet undeveloped deposits. However, continued research and development is needed to support trials of ISR for gold and other precious metals. It is not known yet if gold can be selectively mobilized and recovered during precipitation of contaminant metal sulfides. However, polysulfides are polymers of sulfur and are amenable to advanced formulations may prevent preg-robbing.

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