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IS THERE A GREEN CHEMISTRY APPROACH FOR LEACHING GOLD?

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"Fatma Arslan"
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02/16/2007 09:01 AM

To "James Hendrix" <jhendrix@unlnotes.unl.edu>
cc
bcc
Subject Re: a favor

Dear Prof. Hendrix,

Citation information about your paper:

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We have very nice weather in İstanbul up to now (like spring). We really feel the global warming. I am not sure if I can come to Greece, because my daughter will take the university entrance exam about that time. I would like to be with her. However I always would be happy to see you in Istanbul.

Please say hi to Judy and bring my regards.

If there is anything else, please let me know. I am always happy to know you both.

Best regards,

Fatma
----- Original Message -----
From: James Hendrix
To: arslanf@itu.edu.tr ; hdincer@itu.edu.tr
Sent: 16 Şubat 2007 Cuma 00:36
Subject: a favor

Dear Professors, I hope the weather is treating you well in Istanbul. We have had four weeks of cold weather that makes me wonder if we really have gobal warming.

I am requesting a favor from either of both of you. In 2005 I wrote a paper and then presented it at the XI Balkan Mineral Processing Congress in Albania. I have never gotten confirmation that it was included in the proceedings. I have gone through Google and I see a few people have used the proceedings as a reference so I believe they were published. Hopefully someone in your department has a copy. If so, would you check to see if my paper was included. If it was, maybe I could get the citation information.

IS THERE A GREEN CHEMISTRY APPROACH FOR LEACHING GOLD?

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Over the past fifteen years there has been significant interest in the concepts of sustainable development and mining. Many governments, mining companies and non-government organizations have embraced the concepts of sustainable development. One concept generated from the ideas stemming from sustainable mining is that of 'green gold'. Similar to sustainable mining, green gold's meaning is defined by the originator.

Built into the definition of green gold are the diverse concerns for human well-being, community robustness, environmental integrity, and overall social and ethical responsibility. This paper concentrates on the concerns of environmental integrity. The potential for an alternative to cyanide leaching of gold ores is examined in terms of green chemistry.

Also discussed is the potential of cyanide leaching becoming more environmentally friendly.

The leaching reagents cyanide, thiocyanate, thiosulfate, and thiourea are compared using some of the principles of green chemistry, specifically,

1. prevention,
2. atom economy,
3. safer auxiliaries
4. real-time analysis for pollution prevention.

SUSTAINABLE DEVELOPMENT

Sustainable development is a growing concern expressed by many businesses, organizations and individuals. Yet, no workable quantifiable definition of sustainability is available for evaluation of specific projects or operations. The lack of such a definition inherently gives engineers difficulty. Sustainability of human activities (predominantly production and consumption) is a growing concern among businesses, customers, governments, international bodies and non-governmental organizations. These concerns are often linked to energy efficiency, reduction of environmentally harmful emissions, ecosystem preservation and other "save the Earth" efforts (Hemanowicz, 2004). They are becoming a part of the "triple bottom line" for business accounting: financial, social and environmental (EBF, 2002). Despite its increasing importance, current definitions of "sustainability" are somewhat vacuous. The most commonly accepted description was provided by the World Commission on Environment and Development (1987) in the "Brundtland Report". According to this report, the goal of sustainability is to "meet the needs of the present generation without compromising the ability of future generations to meet their own needs".

SUSTAINABLE MINING

Obviously, sustainable mining is part of the more general notion of sustainable development. But what is it? The definitions and the perceived concepts associated with the term, "sustainable mining" are as diverse and numerous as the special interest groups that use the terminology. How do we recognize sustainable development and mining? When the concepts of sustainable development are applied to mineral resources, there is little agreement on what is to be sustained, and by what means. Without such agreement, sustainable development will remain little more than a slogan of little practical value to public-policy makers. Part of what is missing from most discussion is an understanding of the nature of mineral resources and the dynamics of their development (National Academy of Sciences, 1996). Without this understanding the use of the of sustainable development and mining sustainability becomes phrases that often confuse sustainability with environmental protection and other lofty goals that, strictly speaking, are not required for sustainable operations.

The corporate leaders of the minerals industry have responded to the call for sustainable development. The best source of their response is found in the report of the Mining, Minerals and Sustainable Development Project (MMSD, 2002). In the report they state, "One of the greatest challenges facing the world today is integrating economic activity with environmental integrity, social concerns, and effective governance systems. The goal of that integration can be seen as 'sustainable development'. In the context of the minerals sector, the goal should be to maximize the contribution to the well-being of the current generation in a way that ensures an equitable distribution of its costs and benefits, without reducing the potential for future generations to meet their own needs."

Sustainable development and mining sustainability are supported by four 'pillars'; economic sphere, social sphere, environmental sphere, and governance sphere. Each sphere has a set of guiding principles as indicated in Table 1.

Table 1. Sustainable Development Principles. (from MMSD, 2002).

Economic Sphere

- Maximize human well-being
- Ensure efficient use of all resources, natural and otherwise, by maximizing rents
- Seek to identify and internalize environmental and social costs
- Maintain and enhance the conditions for viable enterprise

Social Sphere

- Ensure a fair distribution of the costs and benefits of development for all those alive today
- Respect and reinforce the fundamental rights of human beings, including civil and political liberties, cultural autonomy, social and economic freedoms, and personal security
- See to sustain improvements over time; ensure that depletion of natural resources will not deprive future generations through replacement with other forms of capital

Environmental Sphere

- Promote responsible stewardship of natural resources and the environment, including remediation of past damage
- Minimize waste and environmental damage along the whole of the supply chain
- Exercise prudence where impacts are unknown or uncertain
- Operate within ecological limits and protect critical natural capital

Governance Sphere

- Support representative democracy, including participatory decision-making
- Encourage free enterprise within a system of clear and fair rules and incentives
- Avoid excessive concentration of power through appropriate checks and balances
- Ensure transparency through providing all stakeholders with access to relevant and accurate information
- Ensure Accountability for decisions and actions, which are based on comprehensive and reliable analysis

- Encourage cooperation in order to build trust and shared goals and values
- Ensure that decisions are made at the appropriate level, adhering to the principle of subsidiarity where possible.

The principles of sustainable mining are well-defined by various groups, but the challenges for meeting the principles are great and complex. Many of the challenges facing sustainable mining are challenges that public opinion makers and government officials will have major roles in overcoming them. As technical leaders and educators we do have influence on how the challenge of mining, minerals beneficiation can be less threatening to the local environment and ecology. We can certainly aid in meeting the challenge of developing an integrated approach to using minerals.

One of the challenges is the large amounts of material involved in large-scale mining and minerals extraction. Although Korte and others (2000) have written about the effects of the cyanide leaching gold recovery process on the environment and the ramifications of it in terms of sustainable mining, some of their conclusions can be easily extrapolated to all large mining operations. Without question their point that the problems arising from the change of the chemistry of million of tons of natural ore during the grinding procedure, producing changes in the bioavailabilities of metals and other substances are not well understood. In the case of phosphate production not only are there large quantities of ore, but large quantities of mineral product that is chemically treated. Their conclusion is that when living in a time where the word "sustainability" has a certain weight, can such operations ever be considered sustainable.

Another is challenge of the significant altering of material by the use of chemicals in the treatment of the ores. The American Chemical Society (ACS) supports the use of the twelve Green Chemistry Principles (Anastas, P. T., Warner, J. C., 1998). Bucknam (2004) points out that four of these principles:

1. prevention,
2. atom economy,
3. safer auxiliaries, and
4. real-time analysis for pollution prevention

provide guidance for sustainable use of chemicals in metallurgical processing.

Mining produces very large volumes of waste, so decisions about where and how to dispose of it are often virtually irreversible. Because decisions about waste handling and other aspects of operations are often so difficult an expensive to reverse, they need to be made correctly in the first place through mine closure planning.

A third challenge is the environmental legacy left by mining. The environmental issues of current mining operations are daunting enough. But in many ways far more troubling are some of the continuing effects of past mining and smelting. The development of an environmental management system (EMS) in which an environmental impact assessment (EIA) is an integral part would permit the mining company and the regulating authority a structure method for having an awareness and control of the performance of a project that could be applied at all stages of the mining life cycle. In the times of sustainable development the EIA is insufficient. Now and in the future there is a greater need for integrated impact assessments. The minimum loss of biodiversity is the other great challenge of mining sustainability. The loss of biodiversity is an irreversible loss. Conservation practices that guarantee a minimum impact on biodiversity must be adopted and implemented.

As important as the methods of mining and beneficiation is how the minerals are used in efforts to develop sustainable development. An integrated approach for the use of minerals must be utilized. The use and downstream supply of mineral products has implications for sustainable development and must be considered along with mining and processing of minerals. Current patterns of minerals use raise concerns about efficiency and the need for more equitable access to resources world-wide. The environmental and health impacts of different mineral products in use need to be carefully managed. Where the risks associated with use are deemed unacceptable or are not known, the costs associated with using certain minerals may outweigh the benefits.

GOLD HYDROMETALLURGY AND CYANIDE

The cyanidation process is remarkably robust and the gold-cyanide complex ion is very stable and gives very few operation problems. In addition to valuable results from research and development, industrial operation experiences have made the cyanidation process a great success. However, the toxicity of cyanide is a concern. With increasing regulations on the use of cyanide and the lowering of acceptable cyanide discharge levels, the gold industry faces more challenges than ever before. Cyanide is unable to effectively extract gold from certain difficult-to-treat ores leading to poor gold recovery from carbonaceous refractory ores and lack of selectivity in the treatment of copper bearing gold ores. In these cases, cyanide consumption is generally high and tailings discharge more difficult.

ALTERNATIVE LIXIVIANTS

Alternative reagents that have been seriously considered include the halide system (chlorine, bromine and iodine), the thiosystem (thiosulfate, thiocyanate and thiourea), and polysulfide system (S_x^{2-}), and the ammonia system (ammonia and ammonium copper-cyanide) (Wan, R. Y., et al, 2005).

In the alkaline copper-ammonia-thiosulfate system most common sulfide minerals which exist in refractory gold ores become unstable in thiosulfate solution under gold leaching conditions. The presence of certain sulfide minerals accelerates thiosulfate degradation, consumes thiosulfate, and retards gold dissolution. Leaching experimental results confirm that thiosulfate is much more stable in the leaching of oxide ores compared to its stability in the leaching of sulfidic and/or carbonaceous ores.

Thiocyanate is an effective lixiviant for gold leaching in an acidic environment. Thiocyanate is a pseudohalide. The pseudohalide behavior of thiocyanate results in the formation of insoluble salts when the thiocyanate reacts with silver, mercury, lead and copper ion under certain conditions depending on the thiocyanate concentration. At low thiocyanate concentrations, the formation of insoluble compounds such as AgSCN and CuSCN may precipitate on the gold surface and retard gold dissolution.

For the ferric-thiourea system, a high reagent consumption and gold passivation make the system impractical for commercial operation.

However the copper-ammonia-thiosulfate process has a number of significant problems which have impeded its implementation industrially. These include (Jeffrey, M. J., et al, 2005):

1. High rates of thiosulfate oxidation in the presence of oxygen (Byerley, J. J., et al, 1975), (Breuer, P. L., Jeffrey, M. L., 2003).
2. Generation of polythionates which hinder the resin adsorption process (Nicol, M. J., O'Malley, G., 2002).
3. The requirement for relatively high concentrations of ammonia, and hence the environmental impact of ammonia/ammonium discharges needs to be considered.

On possible innovation to the thiosulfate process is the application of the ferric-oxalate-thiosulfate process. Studies have been conducted in which the ferric ions stabilized using oxalate was used as the oxidant in the system, and thiourea was used as an additive to improve the leaching kinetics. It was shown that the gold leach rate and solution stability were dependent on the ferric to oxalate ratio, and for a ratio of Fe(III):oxalate of 1:3, the solution E_H and the gold leach rate were stable with time. At lower Fe(III):oxalate, some of the Fe(III) is reactive towards thiosulfate.

Barbosa-Filho and Monhemius (1995) showed that thiocyanate can leach gold in the pH range of 1-3 at higher temperatures (up to 85°C). The low pH and the higher temperatures would indicate that high capital costs would be required for a leach plant. The higher temperatures would also mean that higher operating costs would be required compared to cyanidation. The availability of thiocyanate may also be a restriction and if thiocyanate had to be detoxified, a considerable oxygen demand would be necessary, which would even further increase the operating costs(Gos, S., Rubo, A., 2001).

This lixiviant, however, may be suitable for most ore types and the recyclability could be possible if the temperature is not too high to decompose to a considerable extent. In practice, high temperature around 85°C is, unfortunately, necessary to achieve satisfactory leach performance. An ultimate oxidation cyanate and sulphate is also possible. These costs, however, as already mentioned, would be considerable, since five moles of active oxygen are required per mole of thiocyanate to oxidize it to sulphate and cyanate.

Compared to cyanide, the use of thiocyanate as an alternative lixiviant is probably not economically viable, because of the high temperatures required, even if detoxification costs are not considered. Although specific cases of viability may be possible with high grade concentrates, for example, the operating costs would be the limiting factor for universal applicability.

CONCLUSIONS

After examining the chemical characteristics and the health and safety profiles of the many proposed alternative lixiviants for cyanide it is not suprising that cyanide is still the most common, if not only universally applicable lixiviant for gold bearing ores. The application of green chemistry for the leaching of gold ores becomes more of an engineering problem than a problem directly associated with chemistry. Atom economy, or the use of the minimum cyanide required is one aspect that must be determined if the cyanide pollution problem is to be satisfactorily abated. Atom economy cannot be achieved without real-time analysis for pollution prevention.

Even with the acceptance of cyanide or some other lixiviant for gold extraction the public debate over the social value of any gold mining will not abate. The contentions that gold mining has no social value are not answered by improved use of lixiviants nor are the answers within the scope of this paper.

. REFERENCES

Anastas, P. T., Warner, J. C., 1998.*Green Chemistry: Theory and Practice*, Oxford University Press, New York, p.30.

Barbosa-Filho, A. J., and Monhemius, A. J., 1994. Trans. Inst. Min. Metall, May-Aug, pp. 105-125.

Breurer, P. L. and Jeffrey, M. I., 2003. Copper Catalysed Oxidation of Thiosulfate by Oxygen in Gold Leach Solutions. Minerals Engineering 16(1): 21-30.

Bucknam, C. H., 2004. A Green Chemistry Approach to Mercury Control during Cyanide Leaching of Gold. Preprint 04-101, SME Annual Meeting, Feb. 24-26, Denver, Colorado.

Byerley, J., J., Fouda, S. A., and Rempel, G. L., 1975. Activation of Copper(II) Amine Com0lexes by Molecular Oxygen for the Oxidation of Thiosulfate Ions. Journal of the Chemical Society, Balton Transactions: 1329-1338.

EBF, 2002. CFO Europe: Investors Demand Environmental and Social Reporting. http://www.ebusinessforum.com/index.asp?layout=printer_friendly&doc_id=5392

Gos, S., Rubo, A., 2001. The Relevance of Alternative Lixiviants with Regard to Technical Aspects, Work Safety and Environmental Safety. Cyplus, DeGussa AG, Hanau, Germany.

Hermanowicz, S. W., 2004. Entropy and Energy: Toward a Definition of Physical Sustainability, Presentation at the International Eco-Efficiency Conference: Quantified Methods for Decision Making, Leiden, the Netherlands, April 1-3. 14 pp.

Jeffrey, M. I., Chandra, I., Ritchie, I. M., Hope, G. A., Watling, K., and Woods, R., 2005. Innovations in Gold Leaching Research and Development. *Innovations in Natural Resource Processing, Proceedings of the Jan. D. Miller Symposium,* Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO: 207-222

Korte, F., Spiteller, M., and Coulston, F., 2000. The Cyanide Leaching Gold Recovery Process Is a Nonsustainable Technology with Unacceptable Impacts on Ecosystems and Humans: The Disaster in Romania. Ecotoxicology and Environmental Safety, 46: 241-245.

National Academy of Sciences, 1996. *Mineral Resources and Sustainability: Challenges for Earth Scientists,* Commission on Geosciences, Environment, and Resources, National Academy Press, Washington, D.C.

Nicol, M. J., and O"Malley, G., 2002. Recovering Gold from Thiosulfate Leach Pulps via Ion Exchange. JOM 534(10):44-46.

Wan, R. Y., Miller, J. D., and Li, J., 2005. Thiohydrometallurgical Processes for Gold Recovery. *Innovations in Natural Resource Processing, Proceedings of the Jan. K. Miller Symposium,* Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO: 223-244.

World Commission on Environment and Development, 1987. *Our Common Future.* Oxford University Press, Oxford