FINAL REPORT

1 April 2001 – 31 March 2003

TREATMENT OF CYANIDE SOLUTIONS AND SLURRIES USING AIR-SPARGED HYDROCYCLONE (ASH) TECHNOLOGY

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Submitted to
The Office of Industrial Technologies, Energy Efficiency and Renewable Energy
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Submitted by
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PROJECT TEAM

- The team was directed by Professor J. D. Miller from University of Utah, Department of Metallurgical Engineering. Dr. Miller is an internationally known leader in the field of hydrometallurgy. He is the author of more than 300 technical papers and holder of 24 patents in hydrometallurgy and related fields. Administrative matters were managed by Dr. T. Chatwin, Director of the Utah Engineering Experiment Station. He is a well-known process consultant, who has performed numerous investigations on cyanide use and destruction. Dr. J. Hupka, Research Professor had direct responsibility for research supervision both in the laboratory and in the field. Researchers at the University of Utah included Tao Jiang, Bartosz Dabrowski, and Lukasz Hupka.
- ZPM, Inc. was an industrial sponsor, and is actively engaged in commercialization of Air Sparged Hydrocyclone (ASH) technology in the field of industrial wastewater treatment.
- Elbow Creek Engineering, Inc. was an industrial sponsor. Mr. Michael Botz, principal engineer at Elbow Creek, is a leader in the field of design and installation of treatment plants for cyanide destruction, and he has designed and installed several such plants.
- Solvay Minerals was an industrial sponsor. Solvay manufactures metabisulfite (MBS) and other sulfite chemicals at its soda ash mine in Green River, WY. Solvay sells these products worldwide.
- Professor Doug Halbe was an advisor and is an internationally known independent consultant in the field of gold processing, and serves at the University of Utah as an adjunct professor.
- EIMCO-Baker Process was an industrial sponsor of this study. The EIMCO-Baker Process is an equipment manufacturer and process engineering company, which was formed when Baker Hughes purchased EIMCO.
- Midas Mine, an industrial sponsor, is owned by Newmont Mining Corporation, and is a recently commissioned hi-grade underground gold mine, treating 500 tpd in a conventional cyanidation (CIP) circuit. Because of the high silver/gold grade, high cyanide concentrations exist in the process effluent, making cyanide recovery of particular interest.

Other industrial sponsors included:

- Newmont Mining Corporation - Englewood, CO
- Cherokee Chemical Co. - Vernon, CA
- Placer Dome Inc. - Vancouver, B.C.
- Dawson Laboratories - Salt Lake City, UT
- Earthworks Technology - Winnemucca, NV
- Kennecott Minerals - Salt Lake City, UT

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1. Summary

The two-year Department of Energy (DOE) project “Treatment of Cyanide Solutions and Slurries Using Air-Sparged Hydrocyclone (ASH) Technology” (ASH/CN) has been completed. This project was also sponsored by industrial partners, ZPM Inc., Elbow Creek Engineering, Solvay Minerals, EIMCO-Baker Process, Newmont Mining Corporation, Cherokee Chemical Co., Placer Dome Inc., Earthworks Technology, Dawson Laboratories and Kennecott Minerals. Development of a new technology using the air-sparged hydrocyclone (ASH) as a reactor for either cyanide recovery or destruction was the research objective. It was expected that the ASH could potentially replace the conventional stripping tower presently used for HCN stripping and absorption with reduced power costs.

The project was carried out in two phases. The first phase included calculation of basic processing parameters for ASH technology (see Chapter 3), development of the flowsheet, and design/adaptation of the ASH mobile system for hydrogen cyanide (HCN) recovery from cyanide solutions. This was necessary because the ASH was previously used for volatile organics removal from contaminated water. The design and modification of the ASH were performed with the help from ZPM Inc. personnel. Among the modifications, the system was adapted for operation under negative pressure to assure safe operating conditions (see Chapter 5). The research staff was trained in the safe use of cyanide and in hazardous material regulations. Cyanide chemistry was reviewed resulting in identification of proper chemical dosages for cyanide destruction, after completion of each pilot plant run (see Chapters 6 and 7).

The second phase of the research consisted of three field tests that were performed at the Newmont Mining Corporation gold cyanidation plant near Midas, Nevada. The first field test was run between July 26 and August 2, 2002, and the objective was to demonstrate continuous operation of the modified ASH mobile system. ASH units were applied for both stripping and absorption, to recover cyanide, using the acidification-volatilization-reabsorption chemistry (see Chapter 4). Plant barren cyanide solution was used during the field tests. The original ASH system used for the field tests had been designed and fabricated by ZPM Inc. to remove volatile organic compounds from ground water. The system, even with a number of modifications, could not operate at optimum conditions for cyanide recovery. Reactors and pumps installed in the mobile system only allowed for the treatment of clear solutions, not slurries. Also the original mobile system was limited with respect to Q*, the relative air flow rate, and the extent of recovery in a single stage. Due to the lack of automatic controls, the system required constant supervision of the University of Utah (U/U) team. In spite of these difficulties, application of the ASH mobile system was particularly attractive due to compactness of the apparatus and less than 1 second residence time of the aqueous phase in the cyclones. The performance of the ASH system was evaluated by comparison with theoretical predictions (see Chapter 8).

A second run of the pilot plant, incorporating mechanical and process improvements, was carried out from November 20-23, 2002, also at the Midas Mine. In the first pilot run, pressure build-up was experienced in both the stripping and absorbing cyclones after a few hours of operation. Modifications made to the absorbing cyclone eliminated this problem, and the absorbing circuit operated effectively and without significant problems in the second pilot series. A number of mechanical and process modifications were evaluated for the stripping cyclone circuit, and several of these significantly lengthened the operating period with low-pressure drop across the stripping unit. The low-pressure operating time still remained too short for acceptable industrial use, but evaluation of the results revealed that further modifications were required. Process and equipment modifications for this pilot run allowed operation at a Q* (air:solution ratio) in the stripping circuit of 250. Test runs showed that the *Removal Efficiency* (actual removal divided by the calculated theoretical removal at a given Q*) dropped off significantly at this high Q* value of 250. Analysis of data indicated that this was due to flow restrictions in the cyclone design at the high air flow, and modifications to the cyclone were planned. *Actual Removal* percentages of 40% were obtained at a Q* of 130, and about 44% at a Q* of 250. *Removal Efficiencies* of 85% were obtained at Q* of 130 and 44% for Q* of 250. Details and information from the second Midas pilot plant run are included in Section 8.2.2. of this report.

The third round of field tests took place April 25-May 5, 2003. Due to the potential for industrial application of the ASH technology the third field tests were mainly funded by Newmont Mining Corporation and Placer Dome. The objective was to examine a new ASH stripping design at high performance and with a very low gas flow resistance. As a result, the gas phase could be recycled in a closed system. The permeability of the 2-inch porous tubes used in the stripping ASH unit and the performance of the 6” absorption ASH unit during the second field tests indicated a new design for the 2-inch ASH stripping unit. These changes included a tangential air inlet, larger annular space in the air chamber, and 12 spray nozzles in the casing of the unit. To secure minimal resistance to the flow of the gas phase, the traditional porous tube was replaced with stainless steel mesh. A tangential air inlet provided more uniform flow of gas through the mesh. Additionally, a two stage stripping arrangement with one absorption stage was tested.

Chapter 9 of this report includes a summary of estimated capital and operating costs and a preliminary economic analysis for cyanide recovery for two operating mines: Newmont's Midas Mine and Hecla Mining Company's San Sebastian Mine in Mexico. The chapter includes also some other advantages related to the recovery of cyanide with ASH technology.

2. Introduction

The ASH, originally developed at the University of Utah for flotation of fine particles in the mineral industry, has been used for the removal of oil from contaminated soil, for the removal of volatile organic compounds (VOC's) from water, and for the treatment of industrial wastewater [1-3].

A schematic drawing of the ASH unit is presented in the Figure 1. The ASH unit consists of two concentric vertical tubes and a conventional cyclone header at the top. The porous inner tube is constructed of plastic, ceramic, or stainless steel and allows for the sparging of air, or other fluids. The outer nonporous tube holds air jacket and provides for the even distribution of air through the porous tube. In the case of VOC contaminated water, the water is fed tangentially at the top through the cyclone header to develop a swirl flow adjacent to the internal surface of the porous tube, leaving a gas core centered on the axis of the ASH unit.

The high-velocity swirl flow shears the sparged air to produce a high concentration of small bubbles. Intimate interaction between numerous fine bubbles and the contaminated water results in stripping of volatile compounds and their transfer to the vapor phase, which is then transported radially to the center of the cyclone. The major portion of the vapor phase moves towards the vortex finder of the cyclone header, and is directed to an appropriate post-treatment step (absorption or destruction units). Water stripped of HCN and any other volatile compounds is discharged as an underflow product into a receiving tank:

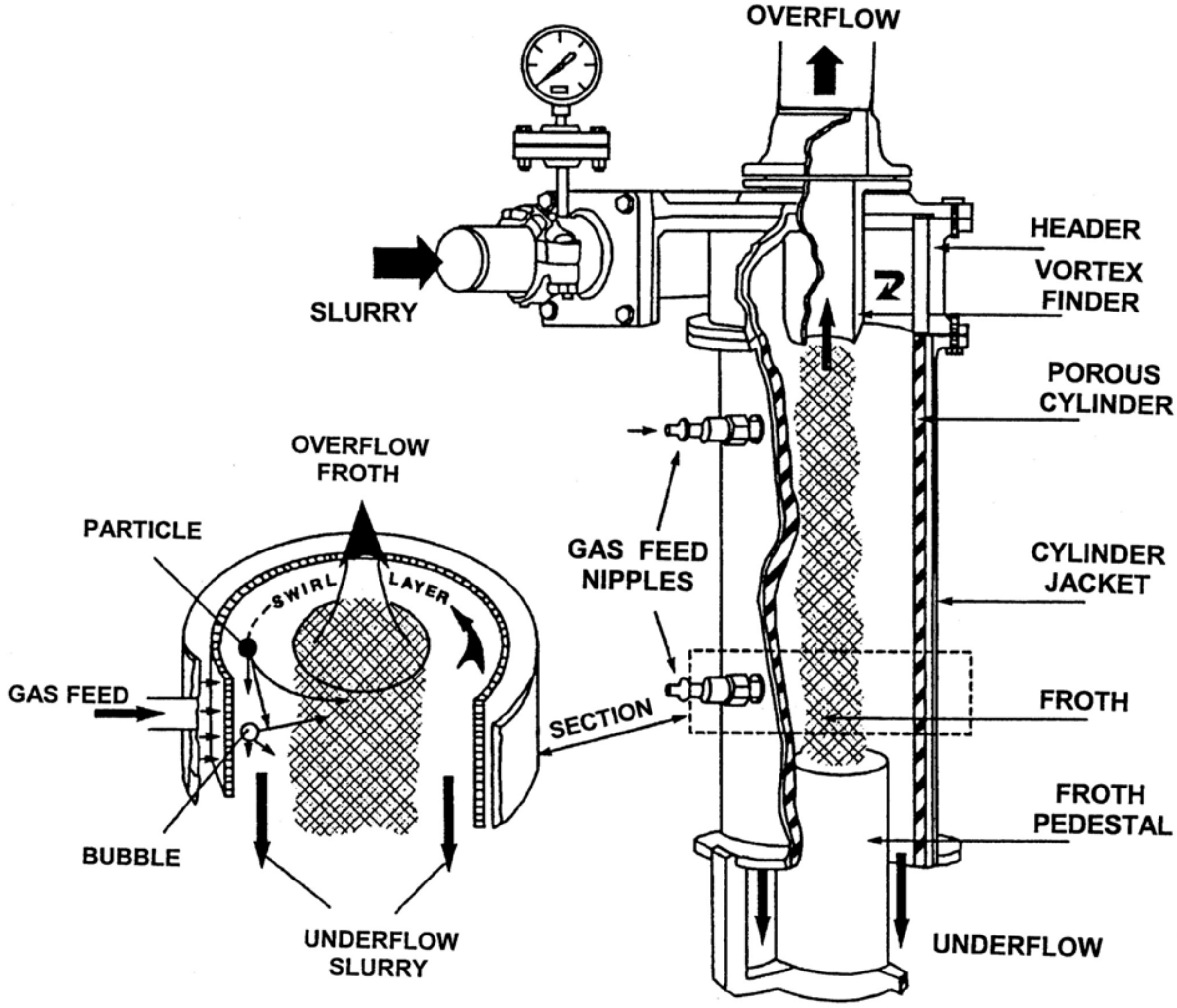


Figure 1. Air-Sparged Hydrocyclone construction and operation mechanism

J. D. Miller and his co-workers at the University of Utah extended the ASH applications to environmental problems such as removal of oil from contaminated soil [1, 3-5], removal of volatile organic compounds (VOC) from water and treatment of industrial wastewater [3, 6-8].

The removal efficiency in the ASH for different organic compounds with respect to their Henry's constants is presented in Figure 2 [8]. It is shown that for compounds of relatively low volatility (methanol and acetone) efficient removal requires a high air/water ratio (Q*). For example only about 4 % of methanol and about 25 % of acetone was removed by stripping for Q* of 33 at 25 °C, while almost 80 % of trichloroethylene (TCE) was stripped under the same conditions. Thus stripping is and extremely efficient method for treatment of solutions containing compounds of high volatility. This plot also shows how much the removal efficiency is changed by the influence of temperature. Since Henry's constant increases with an increase in temperature, greater removal of the solute is achieved at higher temperatures. For instance by changing the temperature from 24 to 60 °C, the removal efficiency of TCE increased by 17 % on average. It should be noted that HCN with a Henry's constant of about 0.0058 at 25 °C has been included in the plot. Based on the stripping of VOC's it can be expected that a large Q* value will be required for removal of HCN.

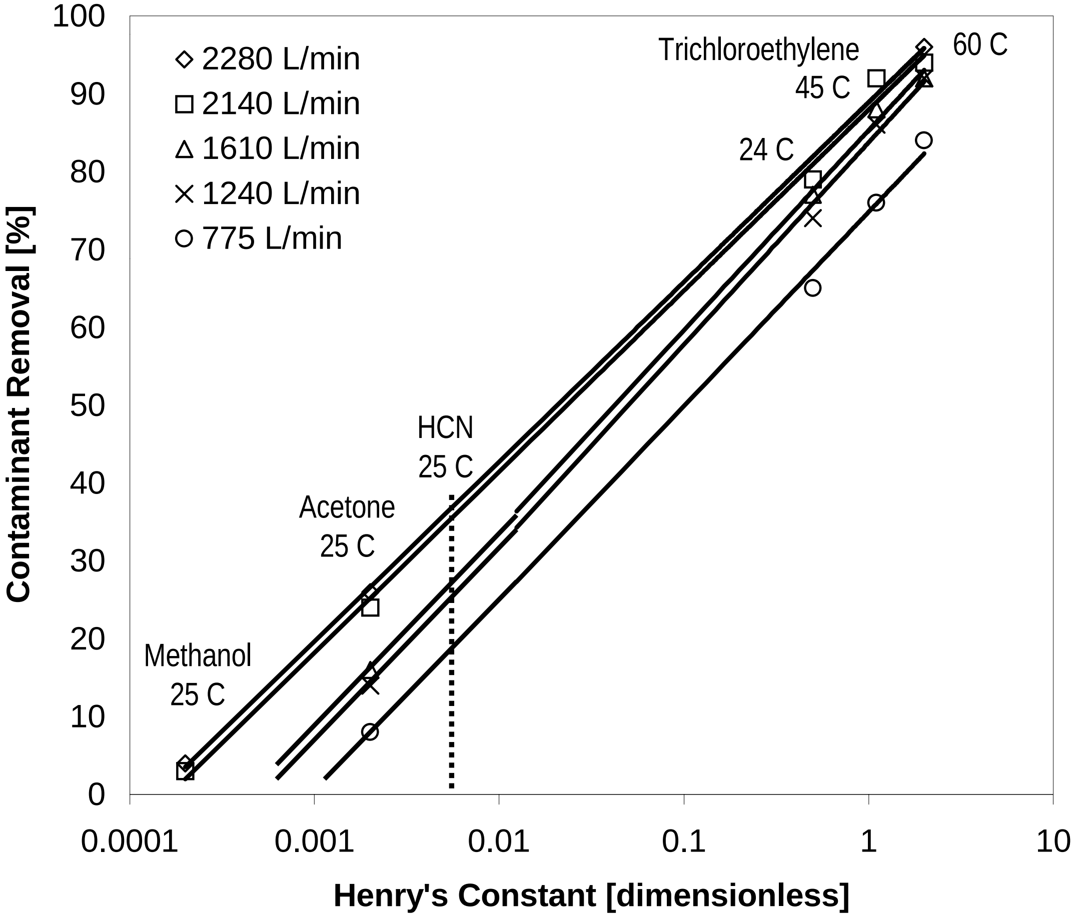


Figure 2. Contaminant removal efficiency for different air flow rates and constant water flow rate 70 L/min as a function of Henry's constant.

3. Henry's Constant and Q* for HCN Stripping in the ASH

In general the basic principle which governs air stripping is Henry's Constant (H_c), which defines the partition of a volatile solute (HCN in this case) between the solution and gas phases.

Henry's constant can be dimensionless, or carry units such as defined from Equations (1) and (2):

$$H_1 = \frac{P_{HCN}}{X_{HCN}} \quad \text{[atm/mole fraction]} \tag{1}$$

where P_{HCN} = partial pressure of HCN above a liquid
X_{HCN} = mole fraction of HCN in a liquid

$$H_2 = \frac{P_{HCN}}{C_{HCN}} \quad \text{[atm m}^3\text{/mole]} \tag{2}$$

where C_{HCN} = concentration of HCN in a liquid

Since

$$C_{HCN} = X_{HCN} \cdot \frac{10^6}{18} \tag{3}$$

it can be shown that:

$$H_2 = H_1 \cdot \frac{18}{10^6} \tag{4}$$

Also

$$H_c = \frac{H_2}{RT} \tag{5}$$

where H_c = dimensionless Henry's constant
R = universal gas constant
T = absolute temperature

Then by combining equations (4) and (5):

$$H_c = \frac{18H_1}{10^6 \cdot RT} \tag{6}$$

In the case of HCN, H_c values are listed in Table 1.

Table 1. Henry's constants for HCN at room temperature as reported in the literature.

H_1 atm/mole fraction	H_c dimensionless	Reference
7.24	0.0054	[9]
6.40	0.0048	[10]
6.10	0.0046	[11]

3.1. Predictions of Air to Water Ratio (Q*) from Henry's Constant

The mass balance equation for continuous stripping at steady state can be written:

$$Q_W\left(C_{in}-C_{out}\right)=Q_A\left(A_{out}-A_{in}\right) \tag{7}$$

where Q_W and Q_A are the flow rates of solution and air respectively, C_{in} and C_{out} the concentrations of cyanide in the solution before and after stripping, and A_{in} and A_{out} are the HCN concentrations in air before and after stripping.

When A_{in} is equal to 0, A_{out} is determined when equilibrium is achieved, which from Henry's law, using the dimensionless Henry's constant (H_c), is:

$$A_{out}=H_c\cdot C_{in} \tag{8}$$

Substitution of Equation (8) into Equation (7) gives Equation (9) and (10):

$$Q_W\left(C_{in}-C_{out}\right)=Q_A H_c C_{in} \tag{9}$$

$$\frac{Q_A}{Q_W}=\frac{\left(C_{in}-C_{out}\right)}{H_c C_{in}} \tag{10}$$

Therefore, the theoretical minimum air/liquid ratio $Q^*_{\min}$ should be:

$$Q^*_{\min}=\frac{Q_A}{Q_W}=\frac{\left(C_{in}-C_{out}\right)}{H_c C_{in}} \tag{11}$$

or

$$Q^*_{\min} = \frac{X_R}{H_c} \tag{12}$$

where X_R is the theoretical fraction of cyanide removed of cyanide in a single stage

Assuming 100 % HCN removal in a single stage, the theoretical minimum air/water ratio (Q^*_{min}) for HCN stripping can be calculated as shown in Table 2. The results in Table 2 indicate that complete removal of HCN can be expected in one step only when the actual air/water ratio (Q^*_{act}) is greater than about 200.

Table 2. Theoretical minimum of air/water ratio (Q^*_{min}) for complete HCN stripping at room temperature (20°C).

H_c	0.0054	0.0046	0.0048
Q^*_{min}	184	219	209

If the actual air/water ratio is smaller, then multi-stage stripping is necessary for complete HCN removal. For incomplete removal, C_{out} is not equal to 0 and X_R is less than 1. If the air/water ratio and H_c are kept unchanged in each stripping step, X_R will be constant. The total removal (X_T) by stripping in n stages will be:

$$X_T = 1 - \left(1 - X_R\right)^n \tag{13}$$

The required stripping steps can be calculated from Equation (13) for a given single stage removal and the desired overall extent of removal. For example, if an effluent concentration of 4 ppm CN is desired from a feed containing 400 ppm CN, then the total removal, X_T, is 0.99 (99%).

If $Q^* = 100$,

then, $X_R = Q^* H_c = 100 \cdot 0.0048 = 0.48$,

and $n = 7$

In the same way if $Q^* = 150$ then $n = 4$.

Calculations show that the required stripping stages quickly increase with a decrease in the air/water ratio. As shown above, 7 stages are required if Q^*_{act} is kept at 100, while 4 stages are needed for a Q* of 150 at room temperature.

3.2. Factors Affecting HCN Stripping

The Henry's Law constant for HCN is significantly affected by temperature. The precondition to investigate the effect of temperature on Q* is to know Henry's constant at elevated temperatures or the relationship between Henry's constant and temperature. The Henry's constant dependence on temperature for HCN is reported in the literature [12]:

$$\ln H(T) = 9.5850 - 0.03147T + 3.1704\ln T - \frac{6302}{T} \quad \text{for } 273\text{ K} < T < 373\text{ K} \qquad (14)$$

where the dimension of H is in kg·atm/mole. The dimensionless constants for HCN and the Q^*_{min} required at different temperatures were calculated using Equation (12) and (14), and are presented in Table 3.

Table 3. Dimensionless Henry's constants and Q^*_{min} calculated for different temperatures.

Temperature [°C]	H_c	Q^*_{min}
20	0.0018	553
30	0.0029	346
40	0.0044	228

It is clear that these calculated values of H_c are much smaller than reported ones (0.0046 to 0.0054 at 20 °C) as stated above. This indicates that Equation (14) is not able to correctly elucidate the effects of temperature on Henry's constant for HCN. Some authors proposed the following equation to describe the effects of temperature on Henry's constant [13]:

$$H = e^{\left(A - \frac{B}{T}\right)} \quad [\text{atm m}^3/\text{mole}] \qquad (15)$$

where A, B = regression coefficients
T = absolute temperature

However, Henry’s constants for at least two different temperatures must be known in order to obtain the regression coefficients. It is reported [13] that the Henry's constant may be estimated from Equation (16):

$$H = \frac{p}{S} \qquad [\text{atm m}^3/\text{mole}] \tag{16}$$

where p = partial vapor pressure
S = solubility

From the literature [14], the vapor pressure of HCN is 1 atm at 25.9 °C and 2 atm at 45.8 °C. However, the solubility of HCN at these two temperatures is not available. But knowing that HCN has a great solubility in either cold or hot water we can assume that the solubility of HCN does not change too much with temperature in a relative narrow temperature range (20 to 50 °C). Thus, we have:

$$\frac{H_{T2}}{H_{T1}} = \frac{p_{T2}}{p_{T1}} \tag{17}$$

Combining Equation (15) and (17) leads to:

$$\frac{H_{T2}}{H_{T1}} = \frac{p_{T2}}{p_{T1}} = \exp\left[\left(A - \frac{B}{T_2}\right) - \left(A - \frac{B}{T_1}\right)\right] = \exp\left[B\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{18}$$

Substituting T_1 (299.1 K), T_2 (319 K), p_{T1} (1 atm), and p_{T2} (2 atm) into equation (18), the value for B is obtained, B = 3323. Then substituting the H value at 20 ^{o}C (0.0048 = $1.15 \cdot 10^{-4}$ atm m^3/mole) and the B value into Equation (15), the coefficient A can be obtained (A = 2.2643) and the relation between temperature and Henry's constant for HCN can be expressed by:

$$H = e^{\left(2.2643 - \frac{3323}{T}\right)} \tag{19}$$

Therefore, based on Equation (19), the Henry's constants and Q^*_{min} required for HCN stripping at different temperatures were calculated and are presented in Table 4.

Table 4. Henry's constants and Q* for HCN at different temperature.

Temperature [^{o}C]	H_c	Q^*_{min}
20	0.0048	208
30	0.0067	149
40	0.0092	109
50	0.0124	81

It is evident from Table 4 that the Henry's constant for HCN increases markedly and the required Q^*_{min} decreases quickly with an increase in temperature. For example with an increase in temperature from 20 ^{o}C to 40 ^{o}C the volume of the gas phase required for stripping is cut in half. Such temperature changes can be possibly experienced in the field, thus significant variation in stripping performance of the cyanide recovery system can be expected with variation in temperature.

4. The Process of Cyanide Recovery

The Air-Sparged Hydrocylone (ASH) System applies Acidification Volatilization Re-absorbtion (AVR) chemistry, which has been used in packed towers. In this regard the AVR process is described below in section 4.1 and its accommodation with the ASH system is briefly described in section 4.2.

4.1. Acidification Volatilization Re-absorbtion (AVR) Process

In the handling of cyanide solutions, significant efforts are taken to ensure that the pH is always kept in the alkaline range so that toxic hydrogen cyanide gas will not be released. The AVR process runs directly counter to this principle. The pH of a cyanide solution is lowered by addition of sulfuric acid so that hydrocyanic acid is formed and HCN gas is released (see Figure 6, p.27). This gas can then be absorbed into a sodium hydroxide solution (see Equations 20 and 21):

$$CN^-_{(aq)} + H^+_{(aq)} = HCN_{(g)} \tag{20}$$

$$HCN_{(g)} + NaOH_{(aq)} = NaCN_{(aq)} \tag{21}$$

The AVR process has generally been applied to clear solutions. Although, packed tower systems have been designed to handle slurries [15], eventually, they were converted to operate clear solutions, mainly because of plugging problems.

In the AVR process, wastewater containing cyanide is mixed with sulfuric acid, liberating HCN gas. The mixing vessel must be sealed. The liquid stream leaving the reactor is stripped with a current of air in a packed column. The HCN-laden air is absorbed in a second column containing a downward-flowing stream of NaOH solution, forming sodium cyanide. This can be returned to the plant circuit. Lime is added to the detoxified wastewater to neutralize the stripped solution, and precipitate heavy metals. Based on bench-scale tests, total cyanide levels can be routinely reduced up to 99 %. The cyanide recovery is regulated by multiplying stripping and absorption stages or column sizing. No examples could be found in the literature of a current application of this technology in the United States[15]. There is only one working installation located in Cerro Vanguardia, Argentina. An early version of this technology was operated by Hudson Bay Mining and Smelting, Flin Flon, Manitoba (USA) from 1931 - 1978. Four stripping towers were used in series. The cyanide content was lowered from 560 mg/dm^3 to 44 mg/dm^3 and the resulting effluent, which contained copper cyanide, was fed to a copper sulfate plant. The process had a liquid flowrate in the cyanide stripping column of 107 m^3/h and an air flowrate about 525 times greater. This process was also being used in 1984 at a silver mine in Mexico. A more modern version of the process was operated from 1985-1987 at the Beaconsfield gold mine in Tasmania. The system was designed for maximum safety, incorporating an enclosed negative pressure system. Cyanide recoveries of nearly 95 percent were reported [15].

One of the advantages of this technology over the destruction alternative is that cyanide can be recovered for reuse. The economics may be favorable in very remote locations where the costs of cyanide threaten the economics of the mining project. In addition, the potential aquatic toxicity of cyanide oxidation products (cyanate, ammonia, chloramines) does not arise.

The major limitation of the AVR process is that it is a more complex process than the various treatment alternatives. Sealed mixing vessels and packed columns are required. Disadvantages of AVR include the high capital cost for plant construction, and high energy requirements for aeration. All mining operations involving cyanide are operated under alkaline conditions to avoid the evolution of HCN. This process may be perceived as too hazardous because HCN is deliberately generated. It also has not been conclusively demonstrated that this technology can achieve allowable discharge limits for cyanide [15], and it is considered to be unsuitable for producing a final discharge. Further treatment of the effluent would be necessary. The economics may vary depending on the value of the recovered cyanide (mine location and hydrological situation, transport cost of fresh cyanide, eventual degradation cost of cyanide wastewater, environmental regulations). Studies in New Zealand indicated that the AVR process could generate an operating profit of NZ$ 2.15 - 3.20 per ton of ore processed. However, cyanide costs in New Zealand are 3 - 5 times higher than for example those in the United States [15].

4.2. Mobile Air-Sparged Hydrocylone (ASH) System

The mobile ASH system is similar in principle to an AVR installation, but instead of large packed columns working as stripping reactors and absorbing reactors, small hydrocyclones are installed. The ASH technology allows for construction of relatively small mobile units of lower capital cost.

In the case of the ASH unit, acidified cyanide bearing solution is fed tangentially to the cyclone, the solution then comes into contact with small air bubbles generated at the cyclone wall, and the HCN is stripped from the liquid into the gas phase, and finally absorbed in alkaline solution. Initial results revealed that ASH technology is able to perform with efficiency comparable to a conventional stripping tower, with much lower total equipment and operating space requirements [16, 17].

The ASH can be installed in a mobile system consisting of several stages. If used for hydrogen cyanide (HCN) recovery it incorporates three stages, as shown in Figure 3:

1) acidification of the cyanide solution,
2) stripping (volatilization) of HCN in the ASH
3) re-absorption of HCN in an alkaline solution using the ASH.

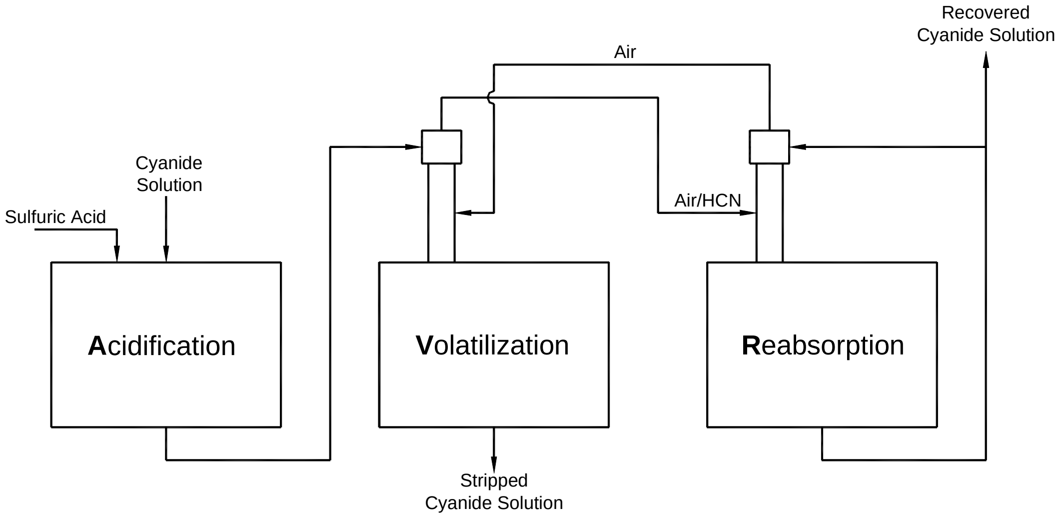


Figure 3. Simplified flowsheet for cyanide recovery using ASH technology.

5. Design and Modification of the ASH System

An ASH mobile system, previously used for the batch removal of volatile organics from contaminated water, was donated by one of the partner companies, ZPM Inc. The ASH system was adapted for HCN recovery from cyanide solutions. Arrangements were made with ZPM Inc. to acquire their mobile plant and the mobile ASH system was transported from Michigan to Utah.

Upon arrival the system was inspected and prepared for modification. Sediments and residues were removed from the tanks, which were then steam cleaned. Modification of the mobile ASH system was initiated by disassembling pipes, the two ASH units and the operating controls. The mechanical condition was evaluated in cooperation with engineers from ZPM Inc. Originally, modification of the ASH mobile system was intended to be accomplished by ZPM at the University of Utah, but to reduce costs, and facilitate the modifications, the ASH pilot plant was transported to Goleta, CA, to be modified by ZPM in October 2001.

The mobile ASH system provided by ZPM Inc. for cyanide recovery and destruction was the most significant in-kind contribution to the project and without which pilot - scale tests could not have been accomplished. The mobile system was originally designed to strip volatile organic compounds (VOC's) from contaminated water. Upon delivery to the U/U in early May 2001, it was discovered that many vital parts and components were missing, other parts were damaged or were worn out. These parts included the pumps, hydrocyclones and piping. Some elements were not necessary for the project (e.g. microwave stimulators), possessed insufficient capacity (e.g. blowers) or were made out of inappropriate materials (flow meters). The tanks were not designed for a negative pressure but for very small positive pressures.

Thus it became obvious that the mobile system required costly and thorough adaptation not originally anticipated. As a consequence, the original process - flow sheet had to be changed several times and the final significant changes were made during the visit of U/U personnel to ZPM Inc. in California, in November 2001. However the system was continuously modified as a result of pilot and field tests (see Figure 4, and Table 5).

The following design decisions were accepted for remodeling of the mobile ASH system.

1. Use 3 existing tanks (total volume:2x220 gal + 1x440 gal) after necessary adaptation.

2. Apply positive and negative pressure to the tanks; monitor temperature in each tank.
3. Use single ASH units and multi-ASH units.
4. Operate the mobile system in the following modes:
    - Single pass for acidification/volatilization (AV) + re-absorption (R)
    - Two ASH units in series for AV + one unit for R
    - Batch system for AVR (recirculating system)
    - Treat CN solution to remove CN in R tank
    - Discharge treated solution to sewer
5. Water flow rate:
    - Single ASH unit, single pass: 1–10 gal/min (special header required)
    - Single ASH unit, recirculating mode of operation: 5–20 gal/min
6. Air flow rate:
    - Single ASH unit, single pass: 30-100 scfm
    - Single ASH unit, recirculating mode of operation: up to 100 scfm
7. Required Q*: min. 200
8. To be used Q*: depends on tendency to foaming and other system properties.
9. The pH range would be pH 2 to 6 for stripping and pH 12 to 14 for absorption
10. Mist eliminators: ≈ 40 cm dia x 25 cm deep cylindrical cartridges, $\Delta p \leq 0.05$ atm (≈ 1 psi).
11. Construction materials for reactors, tanks and piping in contact with solution and mist: stainless steel (resistant to pH = 14) – inspection of welds.
12. Absorption of HCN: ASH unit similar to that used for stripping, use twice as large surface of the porous wall or two ASH absorption units.
13. Volume of solution to be stripped: 200–400 L (50–100 gal)
14. Cyanide concentration in model solution: 400 mg/L (total cyanides used in one test: max. 160 g)
15. Accepted analytical control: *on line* cyanide concentration measurement using cyanide ion-selective electrode in the re-absorption tank, combined with sampling and chemical analysis.

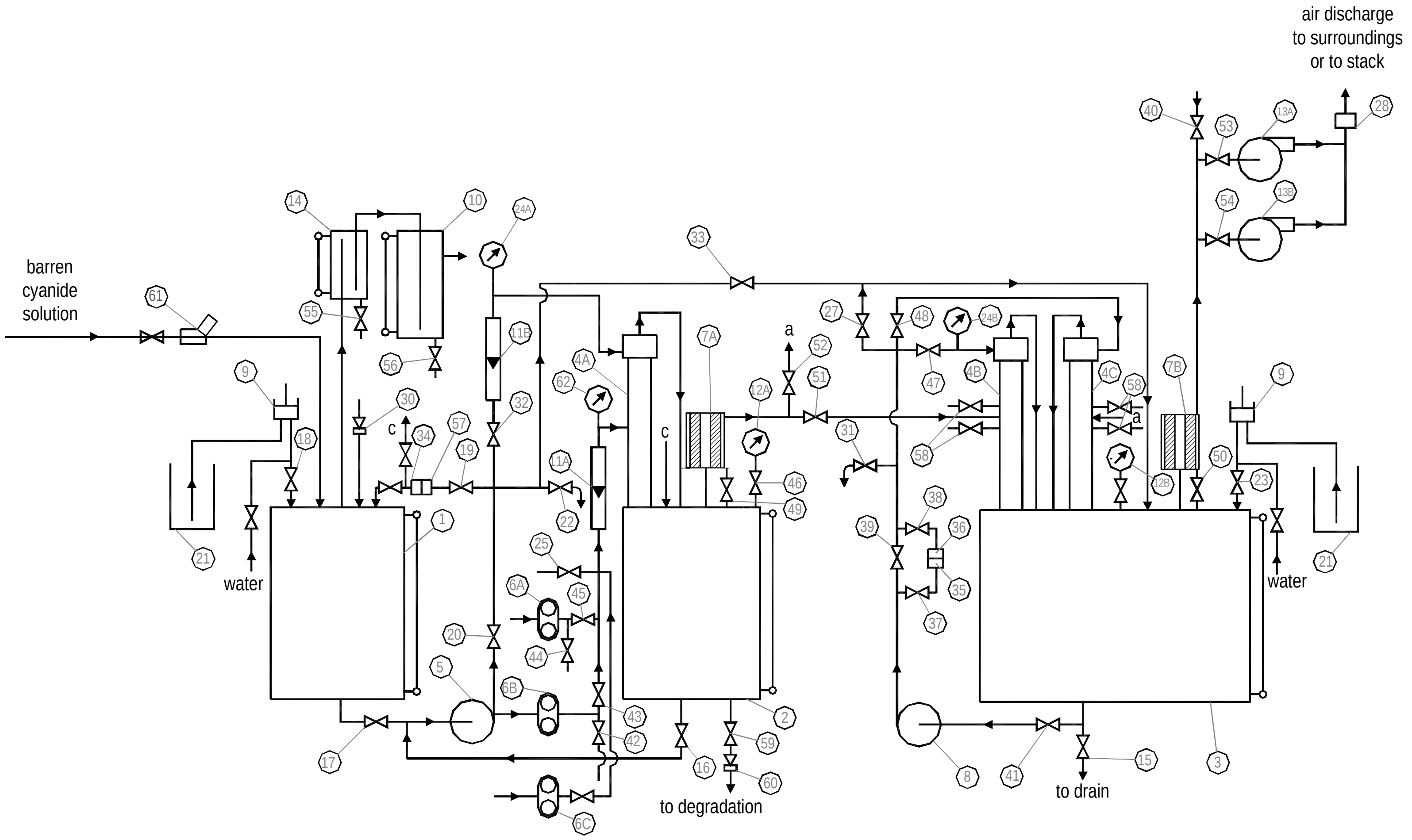


Figure 4. Process flow sheet for mobile ASH system.

Table 5. Major elements of the mobile ASH system, as shown in Figure 4 (most valves omitted).

No	NAME	REMARKS
1	Acidification Tank	220 gal total volume
2	Stripping Tank	220 gal total volume
3	Absorbing Tank	440 gal total volume
4A	Air-Sparged Hydrocyclone	Stripping, custom made header
4B	Air-Sparged Hydrocyclone	Absorbing
4C	Air-Sparged Hydrocyclone	Absorbing
5	Pump	H= 25 mH_2O, Q= 35 gal/min
6A	Blower	Q_{max}= 40 scfm
6B	Blower	Q_{max}= 40 scfm
6C	Blower	External, max 150 scfm
7A	Coalescer - Demister	Air path from stripping tank
7B	Coalescer - Demister	Air path from absorbing Tank
8	Pump	H= 25 mH_2O, Q= 35 gal/min
9	Metering Pump	Q_{max}= 1 gal/min
10	Alkaline Trap	3 gal of 5 % NaOH
11A	Rotameter	To 200 scfm af air
11B	Rotameter	To 40 gal/min of cyanide solution
12A	Mano-vacuometer	U-tube - water
12B	Mano-vacuometer	U-tube - mercury
13A	Blower	$Vacuum_{max}$ = 3 psi
13B	Blower	$Vacuum_{max}$ = 3 psi
14	Stream Breaker	Custom made
21	Container	For chemicals
22	Valve	Sample port
24A	Manometer	Gauge, pressure range 0-15 psi
24B	Manometer	Gauge, pressure range 0-15 psi
25	Valve	Air intake
28	HCN sensor	For HCN monitor in air
31	Valve	Sample port
34	Electrode Port	pH
35	Electrode Port	CN^-
36	Electrode Port	pH
40	Valve	Air intake
57	Electrode Port	Temperature
61	Strainer	60 mesh

It was originally planned that after confirmation of the ASH efficiency and evaluation of the ASH mobile system design and performance at the U/U laboratories, ZPM Inc. would fabricate a new ASH mobile pilot facility, which would be tested at the mine site. Consequently, the ASH mobile system, originally designed for U/U tests, was further upgraded to meet field tests requirements. At the U/U the mobile ASH system was evaluated for both “one – pass” and for a “recirculating – mode” of operation. Plant - site tests were planned for continuous operation of 5 to 6 hours each day. Due to the limitations of reactors and pumps, it was decided that only clear solution, not tailings slurry, would be tested at the plant site.

First trials of water flow and air flow were done to test connections and functions. Subsequent wet tests were carried out by ZPM personnel. All malfunctions were corrected. The second series of wet tests and commissioning was done at the U/U after the mobile system had been returned to Salt Lake City in January 2002 (see Figure 5).

Preliminary wet tests of the refurbished mobile system carried out at ZPM in Goleta, California and later in Salt Lake City at the U/U, showed satisfactory performance regarding the required tightness of tanks 2 and 3, and expected water and air flow rates provided by pumps and blowers. Subsequently detailed wet tests were carried out at the U of U for 2 months using water only and 10 to 20 mg cyanide solutions for total safety. This procedure for cyanide contaminated water allowed us to eliminate leaks, make corrections in piping, move controls and sensors to better locations.

Figure 5. View of the remodelled mobile ASH system during testing of operational procedures at U/U.

6. Safety Issues

Since the project involved dealing with cyanides and there was a risk of hydrogen cyanide leakage, safety was a crucial issue. A number of safety precautions were arranged; beginning from education, through leakage prevention design, ending up with personal safety, monitoring devices and special equipment. Safety issues are discussed in the following sections.

6.1. Toxicity of Cyanides

Hydrogen cyanide or hydrocyanic acid, sometimes called prussic acid, is a very poisonous, colorless gas with a smell of bitter almonds. Its boiling point is 26.5°C, and it is readily soluble in water. It reacts with bases in aqueous solutions to yield cyanides. Neutralization with a base, such as NaOH, produces cyanide salts, such as NaCN. Sodium cyanide and potassium cyanide are important industrial chemicals. Both are used in the cyanide process of separating gold and silver from their ores, in electroplating and in the hardening of steel.

Cyanide ion has a strong tendency to react with metal ions to form stable covalent complexes. Ionic complexes of the types $Au(CN)_2^-$, $Fe\ (CN)_6^{3-}$, $Ag(CN)_2^-$, $Ni(CN)_4^{2-}$ are very common. Organic cyanides are used in the manufacture of several well known plastics, including nylon and orlon, as well as fabrics, synthetic rubber and explosives.

While cyanide solution can be absorbed through the skin or eyes, the primary route of exposure is by inhalation or ingestion [18]. Following absorption, cyanide is distributed rapidly to all organs and tissues in the body. Cyanide combines with ferric iron in the cytochrome - component of the cytochrome oxidase complex in mitochondria - and inhibits this enzyme. This prevents intracellular oxygen use and results in imbalance between ATP hydrolysis and production. Metabolic acidosis is a hallmark of cyanide toxicity and develops as cells are forced to use anaerobic metabolism and accumulate hydrogen ions and lactate.

In acidic solutions cyanides decompose, and highly toxic hydrogen cyanide (HCN) is formed.

$$NaCN + HCl \rightarrow HCN\uparrow + NaCl$$

One of the most important parameters regarding safety in the use of cyanide is to prevent the formation of HCN by maintaining a high pH. The HCN formation diagram is shown in Figure 6. It is necessary to prevent formation of toxic HCN and its release from reactors and/or piping. Therefore, the pH should be kept at a high level, typically pH = 11.

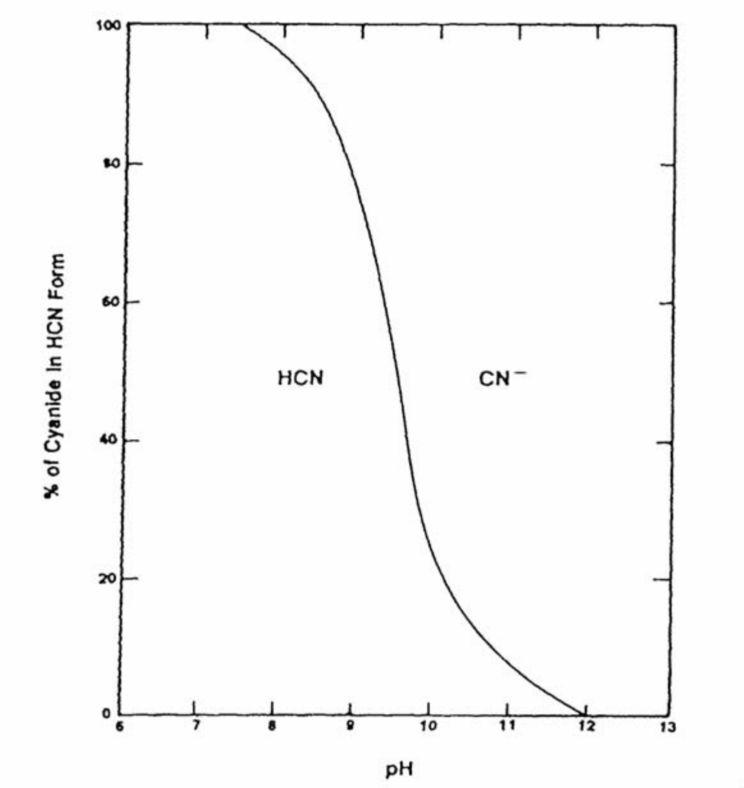


Figure 6. The dependence of HCN formation on pH

The Lethal Concentration (LC_{50}) - concentration-time product capable of killing 50% of an exposed group is 2500-5000 mg·min/m^3 for HCN. The lethal oral dose of HCN and cyanide salts is estimated to be 50 mg and 100-200 mg, respectively. The Lethal Dose (LD_{50}) - dose capable of killing 50% of exposed group - for skin exposures is estimated at 100 mg/kg. Vapor exposures in high concentrations (at or above the LC_{50}) typically can cause death in 6-8 minutes.

Symptoms after high vapor exposure [19]:

- transient hyperpnoea and hypertension 15 seconds after inhalation,
- Convulsions 15-30 seconds later,
- Respiratory arrest 2-3 minutes later,
- Bradycardia, hypotension, and cardiac arrest within 6-8 minutes of exposure.

Symptoms after exposure to lower vapor concentrations, after ingestion or liquid exposure are shown below:

- Transient hyperpnoea,
- Feelings of apprehension or anxiety,

- Vertigo,
- Feeling of weakness,
- Nausea with or without vomiting,
- Muscular trembling,
- Progression of symptoms to unconsciousness,
- Bradypnea followed by apnea,
- Convulsions,
- Cardiac dysrhythmias followed by cardiac arrest.

6.2. Health and Safety Plan

From the beginning of the project safety concerns were given a high priority. Safety rules were established for the research team and for visitors in collaboration with the University of Utah Safety Office. The Occupational Health and Safety Plan was developed for this project, and safety instrumentation and accessories selected and evaluated. A Safety Training Course was developed and delivered to all personnel involved in the research.

The total amount of cyanide to be used in each pilot test with the 2” ASH did not exceed 160 g, since the maximum volume for the test is 400 L and the selected maximum cyanide concentration is 400 mg/L. HCN is very soluble in water, therefore, all hydrogen cyanide released during acidification will dissolve in the aqueous phase without noticeable pressure increase. Only air sparging removes an appreciable amount of HCN from the solution. To stop HCN removal from the acidified solution one only needs to switch-off the stripping blowers. Thus the system is inherently safe in the acidification step. The HCN-loaded air from stripping is directed for absorption into an alkaline solution, while a negative pressure on the system is maintained to prevent any HCN release to the environment.

Major safety measures regarding air and water streams are indicated in Figure 7. A submersible pump is used to empty the sump when necessary to provide additional tank volume to contain any accidental spill.

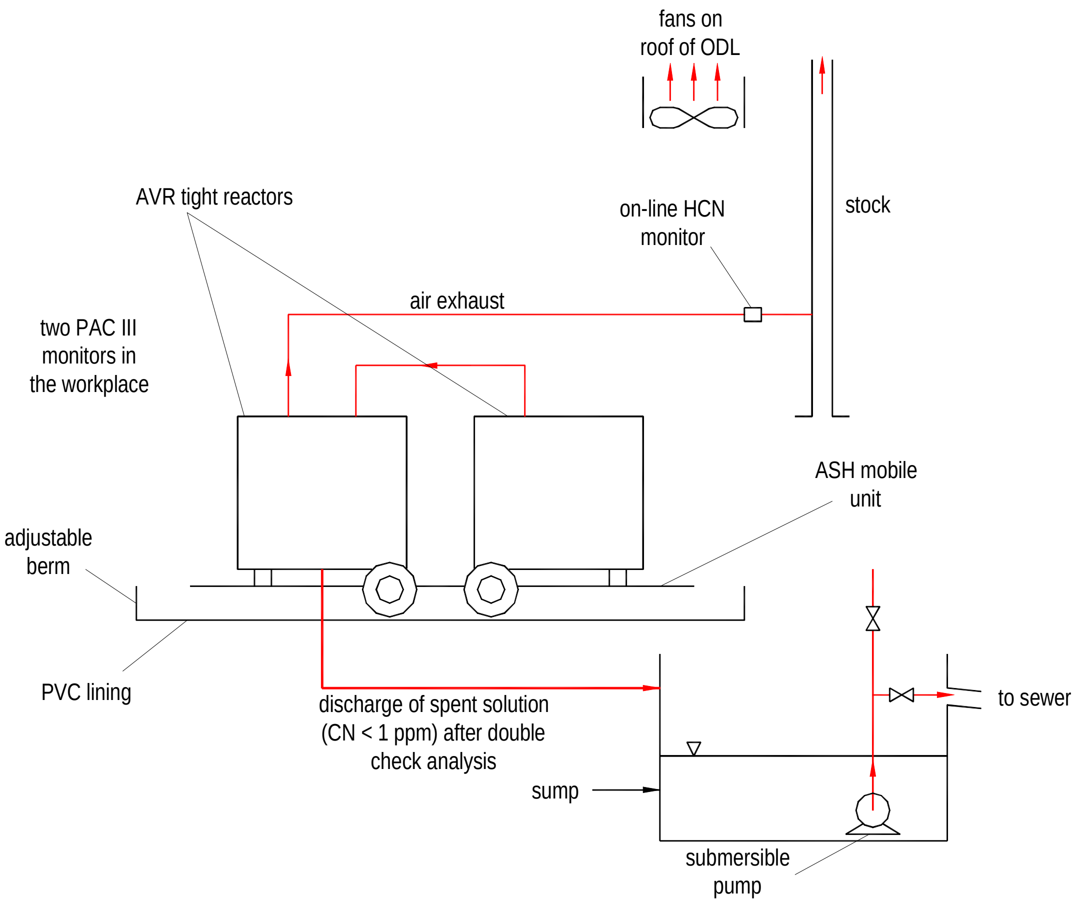


Figure 7. Safety measures undertaken at the pilot plant experiment site (ODL) at the University of Utah

The project Health and Safety Plan was reviewed by the University of Utah Safety Office and U of U Hospital Emergency Management Director.

6.3. Safety Equipment and Devices

The diagram shown in Figure 7 represents the pilot plant together with safety equipment. Protection is provided for personnel, the sewer system and air inside and outside the laboratory. The equipment consists of: a berm preventing spills from the experimental set-up, sump, shower, hydrogen cyanide monitoring instruments, ventilation fans, personal safety equipment, and other safety equipment. Each of the mentioned elements is described separately.

Berm

The berm is a safety reservoir underneath the mobile system. See Figure 8. The berm function is to contain any leaks or spills from the pilot set-up. The berm is constructed in such a way, that it can hold the entire volume of the three tanks. The frame of the berm is constructed from wood beams which are attached to 5 gallon plastic buckets half filled with solidified concrete. Buckets and beams make the adjustable frame easy to dismantle. The frame is covered with thick plastic (PCV) lining, forming a reservoir, resistant to chemicals used in the experiments.

Figure 8. The safety berm underneath the mobile unit prevents any leakage into the sump

Sump

The sump, underneath the mobile unit and the berm, provides additional protection against uncontrollable cyanide discharge into the sewer. In case of a leak from the tanks and/or pipelines, and loss of tightness of the berm, the profile of the floor enables collection of solution in the sump. The sump can accept whole volume of the solution from the tanks. Access to the sump is protected by steel grating. See Figure 9.

Figure 9. Steel grating covering sump. Regular discharge of the spent solution not containing cyanides bypasses the sump and is made directly to the sewer system. The Sump is located underneath the mobile unit. In emergency situations the sump serves as additional protection to prevent uncontrollable cyanide discharge to the sewer

Shower

In case of accidental personal contact with the cyanide solution a safety shower was installed nearby the mobile unit. The shower is equipped with an eyewash fountain and is drained to the sump. Regular shower facilities are available on campus nearby so that the pilot - plant operators can take a shower after working with cyanide solution.

HCN Monitoring Instruments

The mobile system operating team was equipped with two HCN monitors containing electrochemical sensors (PacIII, Drager). The resolution of Pac III for HCN sensor is 0.1 ppm in the air, and the range is 0 to 50.0 ppm. Pac III uses an electrochemical sensor. Electrochemical gas sensors, (often called amperometric gas sensors), have properties that make them attractive for long-term monitoring applications and real-time measurement, process control, and safety applications. A schematic, showing the principle of operation of such a sensor, is presented in Figure 10:

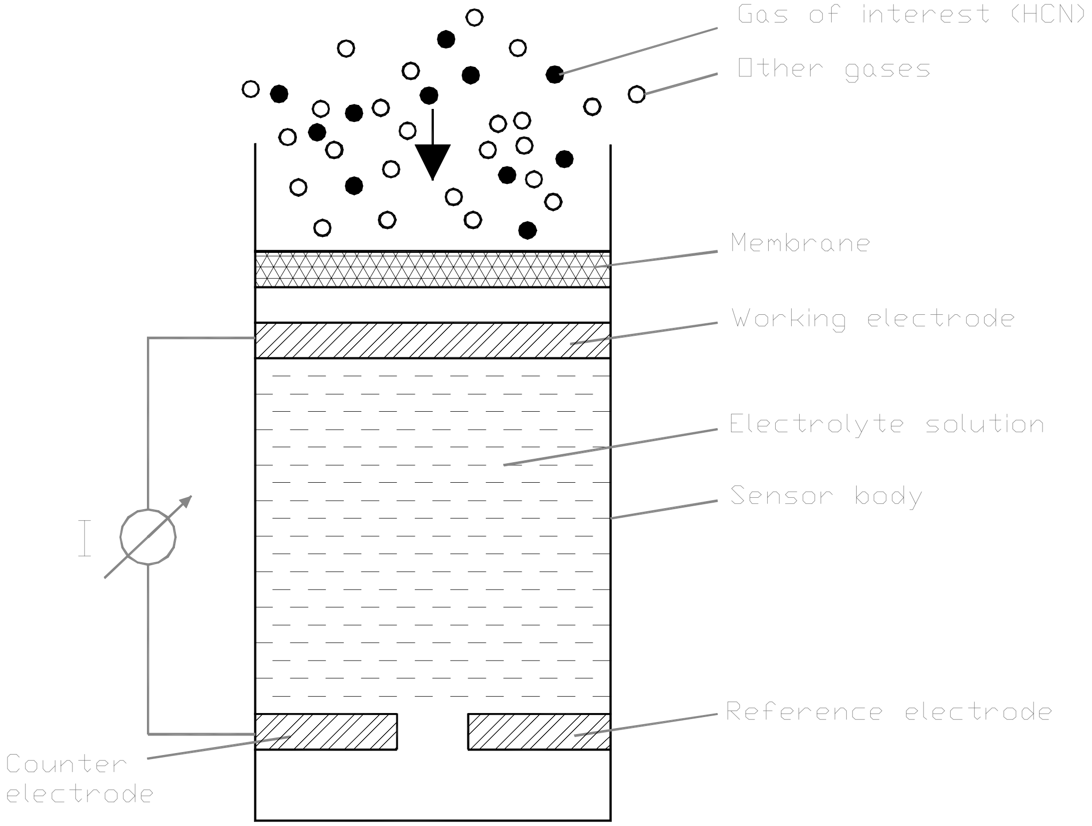


Figure 10. Schematic diagram of a typical, porous-electrode, three-electrode amperometric gas sensor

An amperometric gas sensor (AGS) is an electric generator, oxidizing or reducing traces of electroactive gases to produce a measurable electric current. Gas diffusing into the sensor reacts at the working electrode and generates current flow. Three electrodes are immersed in a suitable electrolyte. The working electrode is made of gold or platinum. For hydrogen cyanide detection the working electrode is usually made of gold. Gold-based sensors also respond to ozone and to nitrogen and sulfur compounds (e.g., NO_2, NO, HNO_3, H_2S, SO_2). Platinum-based sensors respond to all of the gases above, plus carbon-oxygen compounds (CO, formaldehyde, alcohols, etc.).

The working electrode is situated right behind a porous membrane. Gas can diffuse through the membrane, contacting the electrode and electrolyte at the same time. Oxidation or reduction occurs at this point, which results in electrons being left on, or removed from, the electrode. The remaining electrodes (counter electrode and reference electrode) are used to maintain charge balance in the sensor and to control its operation, respectively. The charge differences between the working and counter electrodes can be used to generate an electric current which is the output signal of the sensor. Typically, an external electric circuit is used to amplify the feeble current into a measurable voltage, and to maintain the working electrode at the correct potential for optimum operation.

The selectivity of the two basic sensor types can be modified by changing the potentials applied to the electrodes. The Pac III monitors (Figure 11) have two alarm levels: 10 ppm and 50 ppm.

Safety Ventilation

The stripping operation was design to be inherently safe, and the ASH equipment was thoroughly tested to detect any hydrogen cyanide leakage. Tight containers and piping, and negative pressure under which the system operates ensures safe operation. Nevertheless, two fans in the roof of Ore Dressing Lab (where the mobile unit is situated), were used to ventilate any hydrogen cyanide which might be discharged in case of system failure or operator error.

Personal Equipment

The personal safety equipment (see Figure 11), consists of the following:

- Coverall suit
- Shoe protection
- Eye protection glasses
- Hard hat
- Acid resistant gloves
- Personal Pac III monitor with HCN sensor

Figure 11. Fully equipped pilot plant operator

Other Safety Equipment

Other safety equipment procured included: First Aid Kit, container (20 gallon) for hazardous wastes (cyanide polluted), buckets (5 gallon), liquid soap, paper towels, notebooks – to register visitors to the pilot plant.

6.4. Personnel Safety Course

The use of cyanide requires respect. Hazards can not be underestimated therefore it is important that safety matters were understood and personnel were prepared to handle any emergency. In this regard a personnel safety course was prepared. The objective of the safety course was to train personnel to perform the research in a safe manner, and to prevent any disaster or tragedy. During the course, a description of safety procedures was presented, basic information about cyanides and their properties were provided, and procedures for action in case of emergency were presented.

7. Operation of the Air-Sparged Hydrocyclone (ASH) System

A manual for operation of the mobile system was prepared involving three procedures:

- Preparation of Laboratory
- Cyanide recovery
- Destruction of spent cyanide solution using sodium hypochlorite.

The manual was updated after tests with water then again after using model cyanide solutions. Reading the instructions please refer to the process flow sheet in Figure 4.

7.1. Preparation of the Ore Dressing Lab (ODL) and Auxiliary Facilities

1. Prepare action plan for the entire day.
2. Prepare analytical set-ups for cyanides determination.
3. Restrict access to the ODL placing appropriate signs (with date and time).
4. Check functioning of safety equipment (shower, phone, HCN monitors, emergency spill kit, open entrance gate, put heater on).
5. Attach HCN monitors at designated locations and switch them on.
6. Prepare 2 liters of 25 % NaOH aqueous solution. The alkaline solution should be prepared in a 3 liter beaker, which is placed in a 10 liter PE bucket.
7. Prepare cyanide solution (under the hood), obtained by dissolving 75-200 g of NaCN in 3 liters of alkalized tap water – use 3 g NaOH to obtain pH ~12.5. The cyanide solution should be prepared in a 5 liter container, which is placed in a 10 liter PE bucket.
8. Check position of valves in the mobile system for the selected mode of operation.
9. Place pH and CN^- electrodes in appropriate sockets (35), (36). Open valves (37) and (38) and slightly close valve (39) to allow flow of liquid through the electrode compartment on the feed pipe to the ASH from pump (8)

7.2. Preparation of Model Acidified Cyanide Solution

1. Make sure valves (15), (16), (17) are closed.

2. Fill tank (1) with 100 gal of tap water (connecting hose to pipe (18)), maintaining desired water temperature.
3. Open valves (17), (19),and (20) close (32). Switch on pump (5) to ensure mixing in tank (1). Switch the *on line* pH meter (34) on.
4. Add cyanide solution to tank (1) using metering pump (9). The cyanide solution must be carried from lab 102 to the mobile system in a 10 liter bucket (21) with the cover on. The suction tube of the metering pump must be placed directly in the container with the cyanide solution. After adding cyanide solution put 1 liter of tap water into the container to wash the pump.
5. Acidify the NaCN solution in tank (1) to the desired pH (e.g. pH = 6) by metering 10 % H_2SO_4 solution. After adding acid solution put 1 liter of tap water into the beaker to wash the pump.

7.3. Stripping and Re-absorption of HCN

1. Fill tank (3) with 50 gal of tap water connecting hose to pipe (23).
2. Close valve (33), (47), nad (48) and open valve (27), switch on pump (8) to mix the content of tank (3). Add 25 % NaOH solution to tank (3) using metering pump (9). The alkaline solution must be carried from lab 102 to the mobile system in a 10 liter bucket with the cover on. The suction tube of the metering pump must be placed directly in the beaker with the alkaline solution. After adding the alkaline solution put 1 liter of tap water into the beaker to wash the pump.
3. Open valve (25) and (40), switch on blowers (13A) and (13B), adjust pressure drop in tank (2) and (3) using valves (25) and (40).
4. Open valve (47), (48) and close valve (27), thus directing the alkaline solution to the ASH.
5. Adjust air flow rate using valve (41) and observing pressure gauge (24B), securing slightly negative pressure (0.05 psi) in tank (2). Maximum air flow rate is 100 scfm. A negative pressure in tank (2), controlled by U-tube vacuometer, is required in each HCN volatilization run for safety reasons.
6. Switch the *on line* cyanide concentration meter and pH meter (35), (36) on.

7. Direct HCN-containing solution to the stripping ASH in tank (1) by opening valve (32) and closing to some extent valve (19) in order to achieve the desired water flow rate (between 2 to 5 gal/min). Make sure that air intake valve (30) operates properly.
8. When tank (1) is empty keep pump (5) running and add 10 gal of rinsing water into the tank through pipe (18).
9. Take samples from sample port (31) for chemical analysis regarding total CN^-
10. Switch off pump (5) and (8).
11. Open valve (25), stop blowers (6).

7.4. Disposal of Spent Cyanide Solution

1. Close valves (17), (19), (32) and open valves (16), (20), (33).
2. Switch on pump (5) and empty tank (2) to tank (3). Switch off pump (5).
3. Open valve (27) and close valve (33), (47), and (48). Switch on pump (8).
4. Add 1 gal of NaOCl solution (10-13 % active chlorine) using metering pump (9). Check the pH of the solution in tank (3). It should be ≥ 12. Place the suction tube of the metering pump directly in the container with NaOCl solution. After adding the hypochlorite solution, rinse the pump with water placing the suction hose in a bucket with tap water.
5. Circulate solution using pump (8) until concentration of CN^- is lower than 1 mg/l (which takes ca. 30 minutes).
6. Adjust pH to 8-9 by metering 10 % H_2SO_4 solution using pump (9). The acid solution must be carried from lab 102 to the mobile system in a 10 liter bucket with the cover on. The suction tube of the metering pump must be placed directly in the beaker with the acid solution. After adding the acid solution put 1 liter of tap water into the beaker to wash the pump.
7. Add 1 gal of NaOCl solution (10-13 % active chlorine) using metering pump (28) and circulate the solution for another 60 minutes using pump (8). Place the suction tube of the metering pump directly in the container with NaOCl solution. After adding the hypochlorite solution, rinse the pump with water placing the suction hose in bucket with tap water.
8. Take samples from sample port (31) to double test for cyanide content.

9. Stop pump (8).
10. Open valve (15) to discharge spent solution to sewer when two independent analyses confirm the total cyanide content below 1 mg/l.
11. Clean the ODL and place chemicals in storing cabinets in lab 102. Remove signs restricting access to the ODL.

7.5. In Case of Malfunction

During operation of the system under vacuum no HCN leaks occur. If vacuum cannot be maintained switch off pumps (5) and (8), than switch off blowers (6) and (13). Transfer content of tanks (1) and (2) to tank (3) using pump (5) and proceed according to *Disposal of Spent Cyanide Solution.* Locate the place of a leak and fix the problem. If leaks of a solution occur during a test with cyanide solution first stop pump (5), than pump (8) next switch off blower (6) and (13). Wash contaminated elements of the mobile system with tap water. Add several gallons of bleach into the barn. Transfer solution collected on the barn to tank (3) using metering pump (9). Proceed according to *Disposal of Spent Cyanide Solution.*

Report any malfunction to your supervisor.

8. Investigation of Cyanide Recovery

The cyanide recovery has been investigated at two stages: at laboratory conditions and with a pilot plant scale studies. The pilot plant studies include two phases; the first phase is a research at University of Utah and the second phase are field tests at Ken Snyder Newmont Gold Mine Mill and Cyanidation Plant in Midas, Nevada. The research at mentioned stages and phases is described in this chapter.

8.1. Laboratory Studies

The main objective of laboratory research was to investigate the influence of pH and ionic strength on HCN stripping efficiency and to optimize parameters for cyanide degradation in order to meet discharge criteria (less than 1 ppm of total cyanides) for disposal of spent cyanide solution after stripping experiments.

8.1.1. HCN Stripping

Since previous, preliminary HCN stripping tests [20] in the 2" ASH unit showed a clear dependence of the process efficiency on the solution pH, a laboratory investigation was carried out to confirm such dependency.

Laboratory stripping tests were carried out in a one liter reactor with temperature control, and with an instrumented system to allow for very accurate adjustment of the pH and automatic monitoring of cyanide concentration, see Figure 12. A solution, containing 100 ppm of cyanide was acidified with sulfuric acid to lower the pH and to convert NaCN to HCN gas. After air stripping, the cyanide-laden air was discharged into a sodium hydroxide solution to capture HCN. The investigation was completed for initial pH values of 2, 4, 6, 8, 10, and 12. The data plotted on Figures 13 and 14 shows the stripping efficiency of hydrogen cyanide from solutions of different pH and indicates practically no pH dependence of the process stripping efficiency for the pH range from pH 4 to 8, with about 20 % increased efficiency at pH 2.

In addition stripping experiments for constant pH and different concentrations of sodium chloride were performed. The results are plotted in Figure 15. HCN was stripped from 100 ml solution containing 200 ppm of cyanide for 30 minutes. Experiments were carried out at pH 4, a constant temperature (25 °C) and a constant air flow rate of 1 scfh. Results show a clear dependence of HCN removal on ionic strength (I). Around 60 % more cyanide was stripped when the stripping solution contained 80 % by volume of saturated NaCl. These results are related to an increase in Henry's constant from $H_c = 0.0030$ (for $I = 0.025$) to $H_c = 0.0048$ (for $I = 1.36$).

Although this investigations applies directly only to synthetic solutions with no heavy metals present, the data shows that once the cyanide ions are converted to HCN gas there is no reason (from an economic perspective) for decreasing the pH too far. During stripping the pH did not change except for the almost neutral conditions (pH = 6) due to the loss of the weak acid (HCN). See Figure 14. It should be noted, however, that in the presence of heavy metal ions cyanide complexes (WAD cyanide) low pH values may be required to dissociate the complex and release the cyanide as HCN.

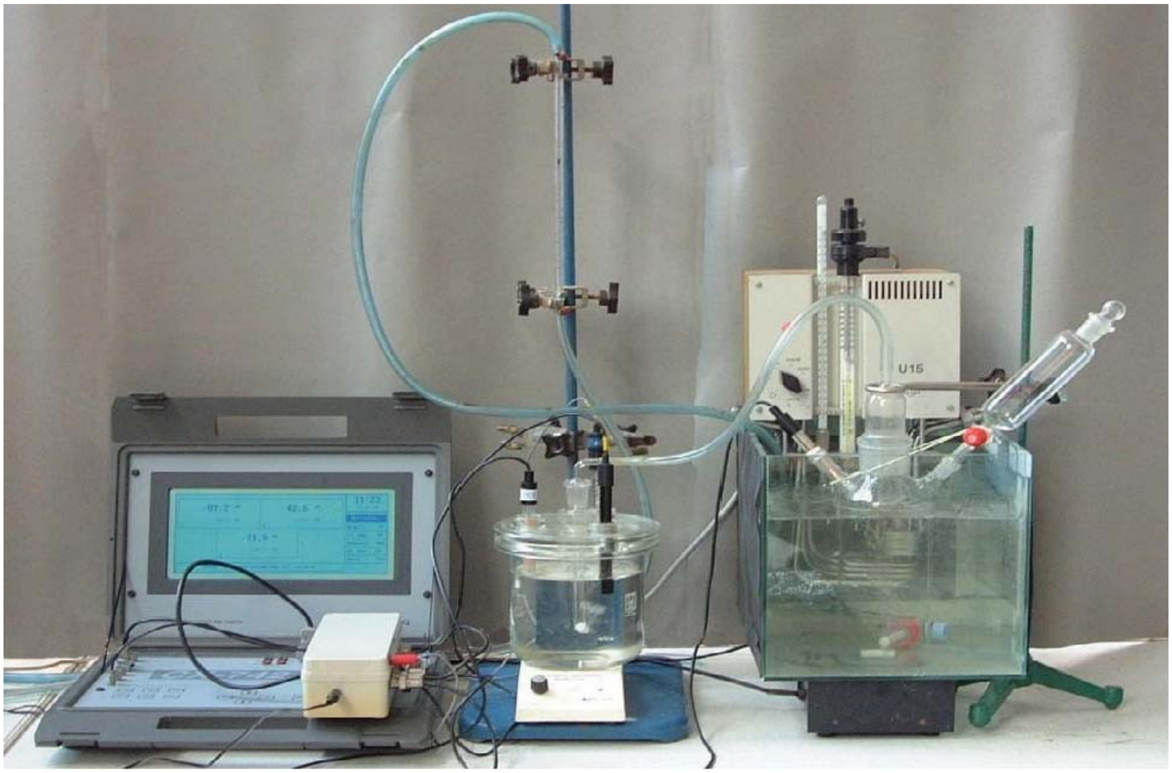


Figure 12. The experimental set-up used for stripping of HCN.

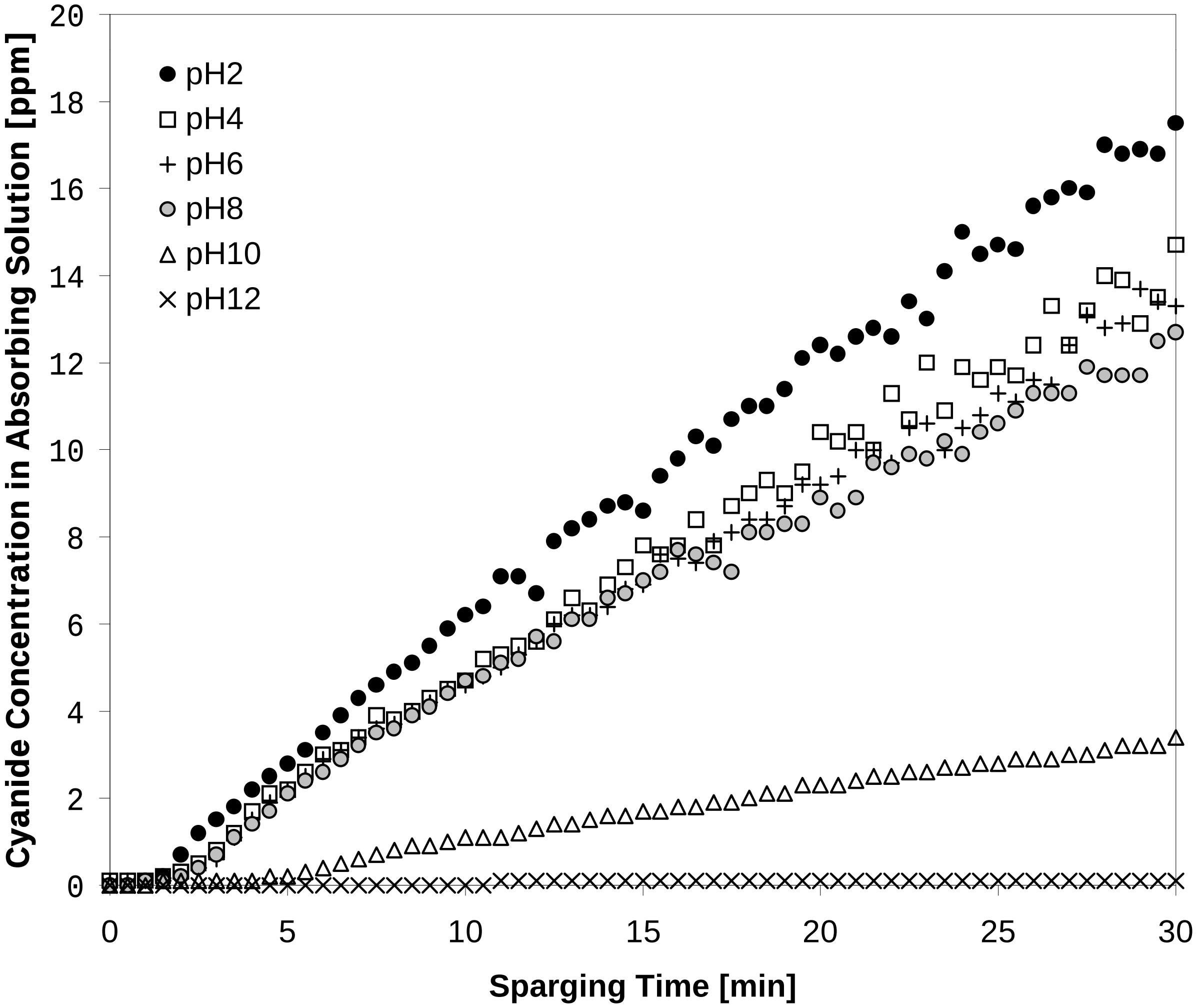


Figure 13. Stripping of hydrogen cyanide from solutions of different pH values (air flow 20 L/hr, room temperature, initial cyanide concentration in stripping solution 100 ppm).

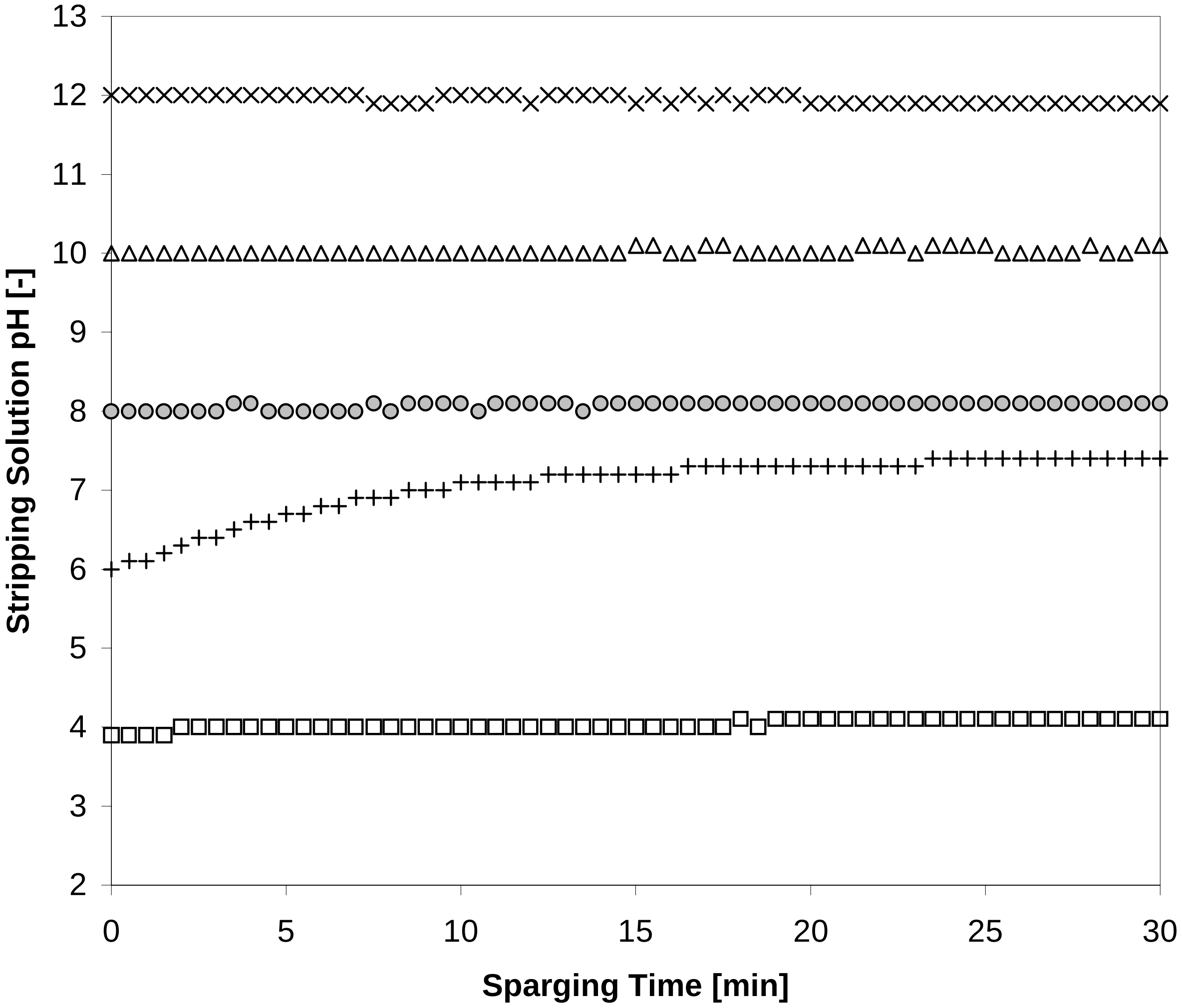


Figure 14. The variation of stripping solution pH during HCN stripping in laboratory experiments.

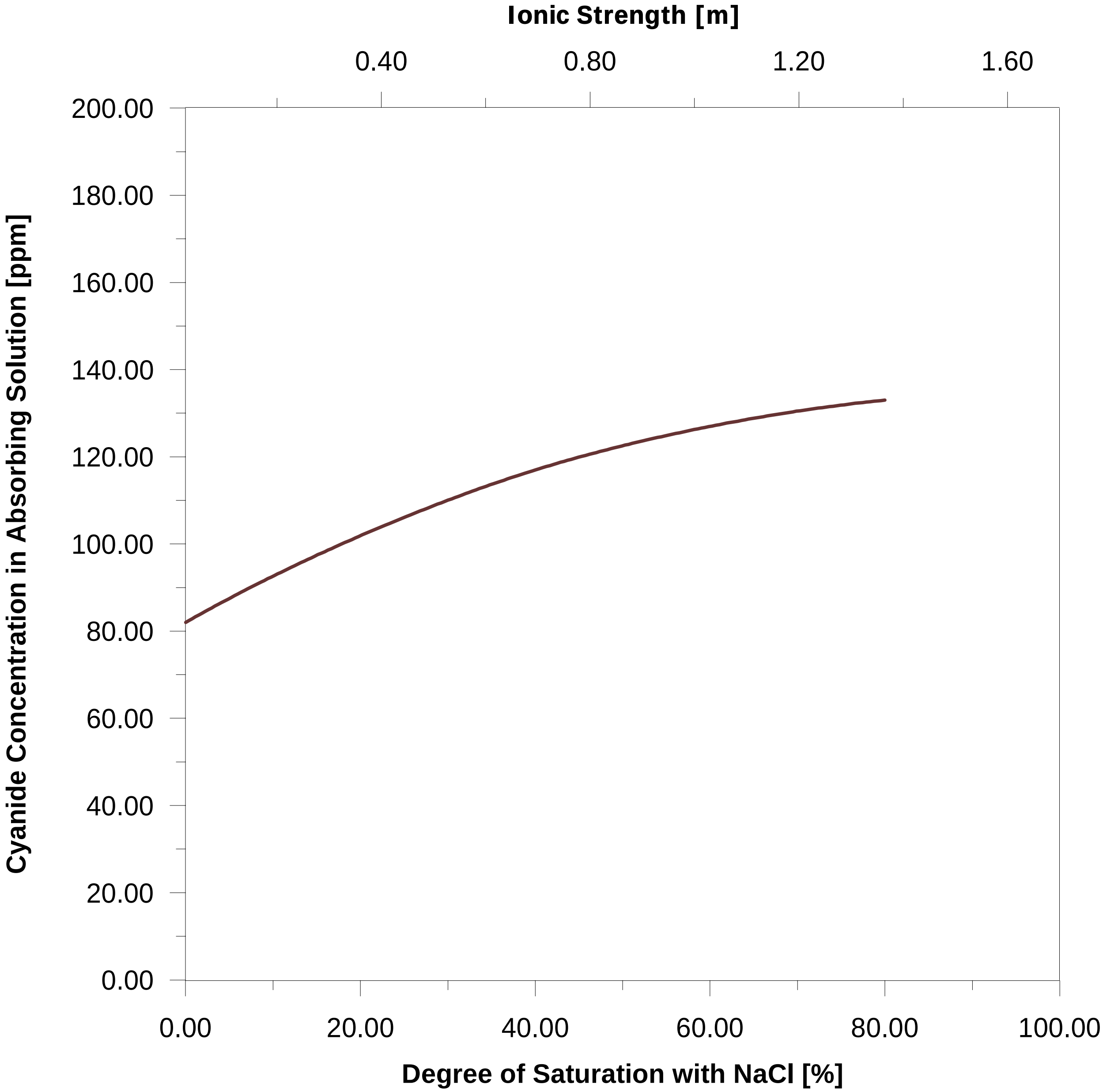


Figure 15. Stripping of hydrogen cyanide from solutions of constant pH 4 and different additions of saturated sodium chloride solution (temp. 25 °C, airflow rate 1 scfh, stripping time – 30 min., initial cyanide concentration – 200 ppm).

8.1.2. Cyanide Degradation

Although many methods are available for degradation of cyanides, alkaline chlorination (method recommended by EPA) was used for treatment of spent cyanide solutions originating from our laboratory and pilot plant research.

Alkaline chlorination is an economical and easily controlled method. In laboratory treatment of waste cyanide solutions chlorine is added as sodium hypochlorite (NaOCl). The treatment of cyanides is accomplished in two stages. The first stage is partial oxidation of the cyanide to cyanate at pH above 9.0 (usually at pH 11) to prevent formation of cyanogen chloride. The second stage is further oxidation of cyanate to carbon dioxide and nitrogen at pH 8.5.

Results in Figure 16 indicate, that efficient oxidation of cyanides can be achieved using a commercial alkaline solution of sodium hypochlorite, *Ultra Clorox Regular Bleach* brand name (The Clorox Company, California, USA). The experiments were carried out in a 800 ml glass reactor. Initial CN^- concentration in distilled water was 100 mg/l and the temperature of the solution was kept constant at 16°C. The temperature, pH and CN^- concentration was monitored *on-line* using automated temperature and pH control, and cyanide ion-selective electrodes. The cyanide solution was circulated by a peristaltic pump through a cell in which the electrodes were placed. The initial pH was adjusted with 1.0 M NaOH and 1ml of Ultra Clorox was added four times every 5 minutes.

After addition of 4 ml of Ultra Clorox (after 15 minutes of the reaction) the cyanide concentration was below 0.1 mg/l regardless of the pH. The results confirmed the theoretical requirement for cyanide oxidation in a model system. Use of tap water may require a slightly greater amount of sodium hypochlorite.

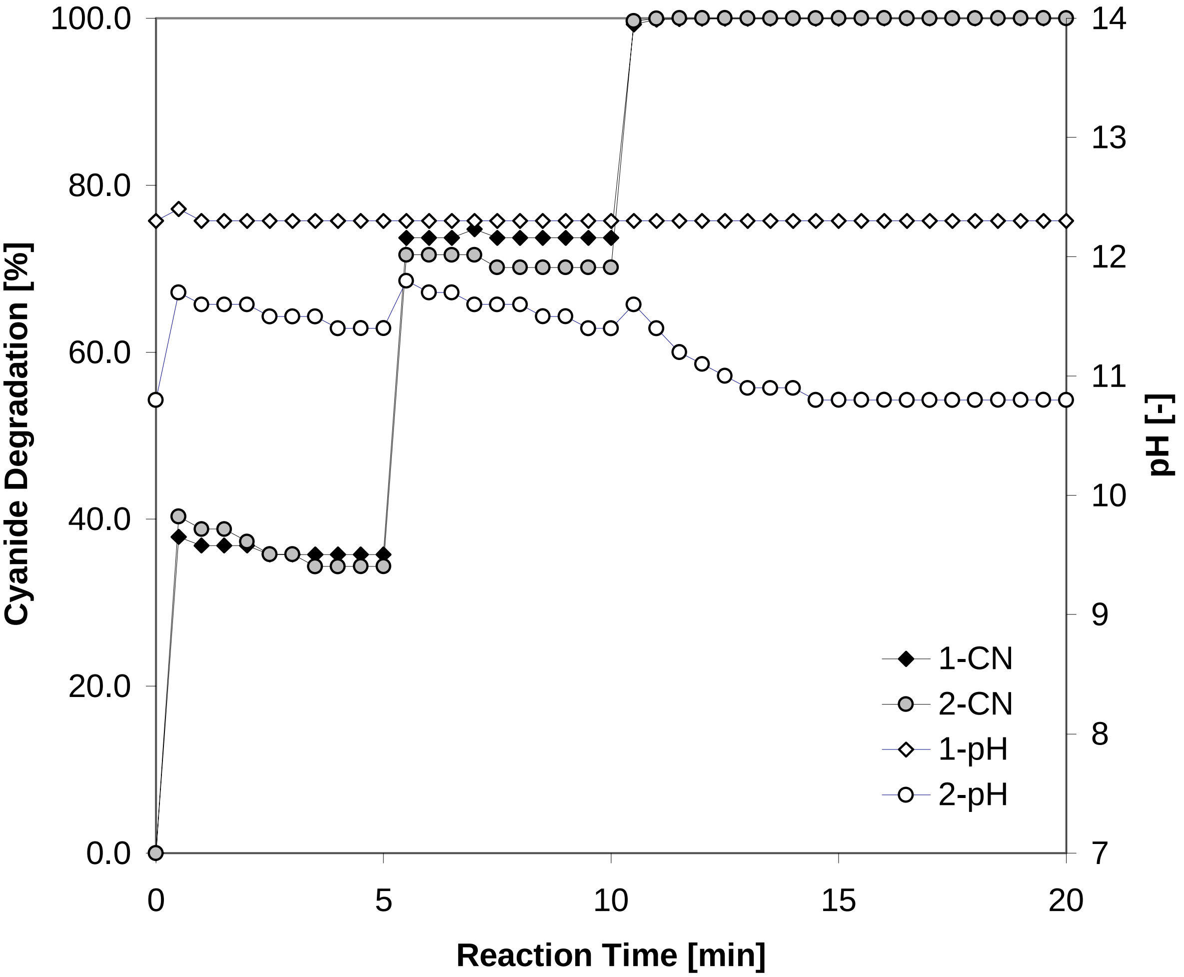


Figure 16. Cyanide degradation in 800 ml laboratory reactor using Ultra Clorox, initial CN^- concentration 100 mg/l.

8.2. Pilot Plant Studies

The pilot plant studies, as mentioned earlier, consist of two phases. The first phase took part in Ore Dressing Lab at University of Utah, where the mobile system was developed, remodeled and tested. The second phase included three rounds of field tests, which were performed at Newmont Mining Corporation gold cyanidation plant near Midas, Nevada. The appropriate modifications resulting from each test were made to the mobile unit. The results and the problems associated with pilot plant studies are discussed in this section.

8.2.1. Model Investigations

The major objective of this task of the Phase I research was to determine whether the ASH system would be superior to stripping and absorption in packed columns. The research program included evaluation of mass transfer coefficients and correlation of the extent of removal with Henry's constants.

An ASH mobile system (see Figure 17), previously used for the batch removal of volatile organics from contaminated water, was obtained from one of the partner companies, ZPM Inc. The ASH system was adapted for HCN recovery from cyanide solutions. Two unit operations, HCN stripping and absorption, were examined employing ASH technology in batch trials using a synthetic CN^- solution. It was found that the ASH under such conditions represents a compact and efficient absorber. In absorption, over 99% of HCN was absorbed; however, the ASH unit, equipped with polyethylene (PE) porous tube was susceptible to plugging. The stripping cyclone showed lower stripping efficiency at low Q* values (60 - 75%) on average. During investigations at the University of Utah, the ASH system was adapted for the first time with negative - pressure conditions. The system functioned well under vacuum, therefore, it was demonstrated that it could be made inherently safe for the workplace.

At the U/U the mobile ASH system was evaluated for both "one – pass" and for a "recirculating – mode" of operation.

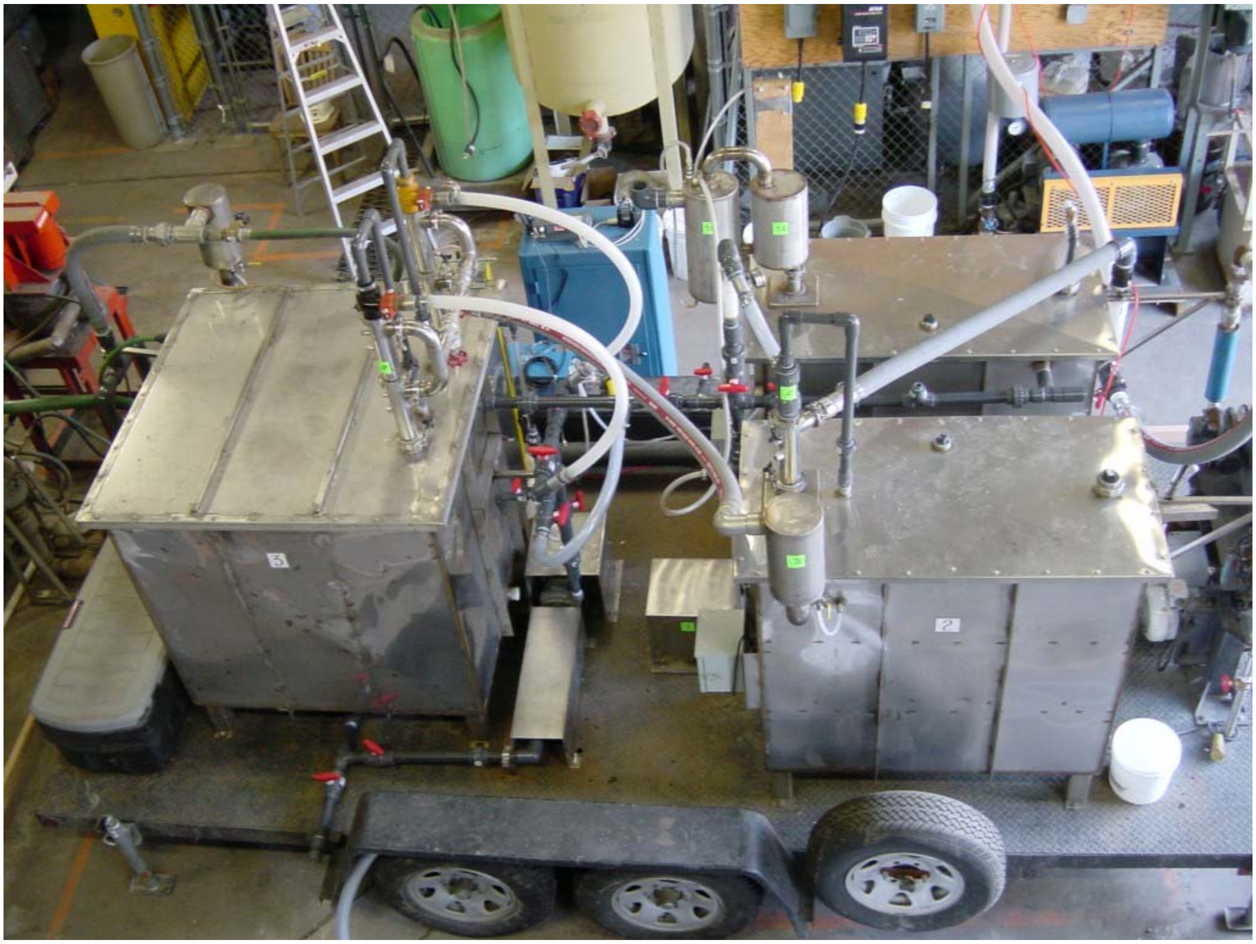


Figure 17. Top view of the remodeled mobile ASH system installed in the Ore Dressing Lab at University of Utah.

During pilot tests at the U/U, the process efficiency was evaluated by comparison of predicted HCN stripping removal with the actual removal obtained for a specific Q*, see Table 6. Thus, the performance of the ASH system could be compared to other stripping equipment.

Table 6. First results of HCN removal from dilute solutions.

No.	Gas Flow Rate [scfm]	Water Flow Rate [gal/min]	Temp. [°C]	pH [-]	Initial CN- Concentr. [ppm]	CN- Concentr. After 1 pass of Stripping [ppm]	Q* [-]	Required Q^*_{min} [-]	Theoretical (Calculated) Removal at actual Q* [%]	Actual Removal [%]	Removal Efficiency [%]
1	50	5.0	18	5.2	22	17	75	229	33	22	67
2	45	5.0	16	4.3	23	19	67	246	27	20	74
3	40	5.0	18	4.0	24	20	60	229	26	16	62

Table 6 shows initial results from the pilot plant tests run, with key data (temperature, initial cyanide concentration, pH, Q*) along with the theoretical removal and the actual removal. The removal efficiency (actual removal/theoretical removal) ranged from 62 to 74%. This is highly encouraging, since it confirms the high efficiency of the ASH unit in this application. Also noted in this table is the fact that Q*'s of over 200 are required in order to obtain 100% stripping.

8.2.2. Field Tests at Ken Snyder Newmont Gold Mine Mill and Cyanidation Plant in Midas, Nevada

The Newmont Midas mine is located about 60 miles by road northeast of Winnemucca, Nevada. The Midas mill treats about 750 tpd of ore with a typical grade of 0.65 oz/t of gold and about ten times that amount of silver. The circuit is a conventional leaching and countercurrent decantation (CCD) circuit, with Merrill Crowe recovery of precious metals. The concentration of WAD cyanide in the barren solution is typically in the range of 400 mg/L. Underflow from the final CCD thickener is treated using the Inco SO_2/Air process to reduce cyanide levels to below 20 mg/L WAD cyanide. Treated slurry tailings are disposed in the tailings pond. Annual gold production is 190,000 oz Au (6 tons), and annual cyanide usage is 290 tons.

Characteristics of the barren solution are presented in Table 7. The barren solution was transparent and colorless. The temperature of the barren solution was constant but ranged form 15 to 32 °C depending on the season.

Table 7. Characteristic of the barren solution.

Measured Parameter	Value
Dissolved solids	6.2 g/l
Total suspended solids	<10 mg/l
Cyanides (AgNO3/rhodanine)	330 - 440 mg/l
Total alkalinity	2200 mg/l CaCO3
Total hardness	2990 mg/l CaCO3
pH	11.1 – 11.2
Temperature	15-20 °C (November), 32 °C (July)

Three rounds of field tests were performed at Newmont Mining Corporation gold cyanidation plant near Midas, Nevada, and modifications resulting from each test were made to the mobile unit.

The first field tests were run between July 26 and August 2, 2002. The mobile system was installed on the concrete delivery load-out adjacent to the thickener floor berm near the CCD circuit and the INCO process reactor, see Figure 18, and Figure 19. The containment area had a sump in the center of the area to pump out any spill. Compressed air was obtained through a high-pressure regulator, industrial water and cyanide barren solutions were available via pressure hose. Barren solution was supplied from the barren pump line located inside the plant. An eye-wash/safety shower was also located nearby.

All water/solution discharges from the system (including caustic cyanide solution at the end of tests) were directed to 1 m^3 PE tank which was placed completely within the contained area, and serviced with a sump pump that pumped directly to the cyanide destruction tanks (The Midas Processing Plant). The PE tank contained caustic to provide pH greater than 10.5, and was emptied when full. Concentrations of cyanide in the alkaline solution after HCN re-absorption were evaluated from 250 ml samples, collected periodically. Samples of the stripped solution were collected in 250 ml PE bottles containing NaOH pellets and analyzed by titration with $Ag(NO)_3$.

The objective of the tests was to demonstrate continuous operation of the ASH mobile system for stripping and recovery of cyanide (the AVR process) using actual barren cyanide solution. Specifically the mobile system was limited with respect to Q*, the relative air flow rate, and the extent of recovery in a single stage.

HCN was removed from the gas phase during absorption with an efficiency exceeding 99 %. The HCN concentration in the discharged gas phase was always less than 10 ppm. No difference in absorption efficiency was observed for medium and fine porous tubes, but fine porous tubes exhibited 3 times greater resistance to gas flow and become plugged faster. HCN re-absorption was carried out in a single ASH. The performance of the unit was exceptionally effective, and the potential of the ASH technology for this application confirmed. Further research on plugging prevention and elimination was undertaken before the second round of field tests.

Figure 18. Ken Snyder Newmont Gold Mine Mill and Cyanidation Plant – cyanide degradation circuit.

Figure 19. Mobile ASH system installed near CCD circuit at the Newmont Mining Corporation gold cyanidation plant near Midas, Nevada.

The stripping *Removal Efficiency,* which is the ratio of the *Actual Removal* to the *Theoretical Removal* reached 40 %, which is 20 % less than the efficiency obtained for model solutions at U/U and for a lower Q^*. It was demonstrated that the mobile ASH system, although designed for batch operation, was successfully converted to the continuous mode of operation for the AVR process.

The second round of field tests took place in November 20-30, 2002, and it was devoted to the scaling problem identification and elimination. As a goal for the stripping circuit was determination of whether the sparger should be made of porous PE tube or other materials, and what should be the size of openings.

The system was operated daily from 6 to 12 hours. Due to winter conditions (frost in the night), time consuming daily preparations (connection/disconnection of electrodes, sensors, instruments, drainage of tanks and pipes in the system and supplying hoses) were necessary. Two centrifugal pumps, and selected valves and pipes were protected from frost damage by heating tape. A submersible pump was placed in the sump in the center of the containment area to pump out any spill.

Low flow resistance for the gas phase in the absorption ASH was essential for maintaining a high Q^*. Minimal resistance to flow was obtained by replacement of the porous tube with stainless steel mesh in a 6'' absorption ASH. Over 95% of HCN was absorbed in one pass after replacement of cyclone insert, but could be suppressed further in a more alkaline environment. Unlike the case for a porous PE tube, the stainless steel mesh was not susceptible to plugging.

Table 8. Processing conditions and efficiency of HCN stripping in the mobile ASH system.

No.	Gas Flow Rate [scfm]	Water Flow Rate [gal/min]	Stripping Temp. [°C]	pH [-]	Initial CN^- Concentr. [ppm]	CN^- Concentr. after 1 pass [ppm]	Actual Q* [-]	Required Q* [-]	Actual Removal [%]	Removal Efficiency [%]
1*	60	3.5	13	4.0	440	265	128	275	40	85
2*	60	3.5	13	4.0	440	265	128	275	40	85
3*	90	3.5	14	4.0	395	245	192	265	38	52
4*	90	3.5	15	4.0	395	235	192	255	41	55
5*	90	3.5	14	4.0	395	235	192	265	41	56
6*	90	3.5	15	4.0	395	255	192	255	35	47
7**	90	3.5	13	4.0	385	245	192	275	36	51
8**	90	3.5	13	4.0	385	260	192	275	32	46
9**	90	3.5	14	4.0	385	240	192	265	38	52
10*	90	3.5	17	4.0	400	240	192	237	40	49
11*	90	3.5	16	4.0	380	210	192	246	45	58
12*	90	3.5	16	4.0	390	230	192	246	41	53
13*	90	3.5	17	4.0	390	220	192	237	44	54
14**	120	3.5	14	4.0	385	220	256	265	43	44
15**	120	3.5	14	4.0	395	240	256	265	39	40
16*	120	3.5	17	4.0	400	215	256	237	46	43

* acidification with H_2SO_4
** acidification with HCl

The HCN stripping efficiency data is shown in Table 8. The data indicates that the maximum *Actual Removal* reached 46 %, which was the highest removal of the HCN obtained in one pass through the ASH. It was expected that changes assuring better aerodynamic flow into the stripping ASH (tangential entry and a larger space between the casing and the porous wall) would improve the efficiency. The kind of acid used had no impact on HCN stripping efficiency.

For a larger Q* (gas phase/liquid phase volumetric ratio) the A*ctual Removal* of HCN from the barren solution was better. Nevertheless, increase of the A*ctual Removal* with increased air flow rate from 60 to 120 was minimal (a few percent). These results indicate that optimum results should likely be obtained by a two- or three-stage stripping system with the Q* in each stage not exceeding 120. This should enable the system to attain the 80-90 % (or higher) overall stripping level necessary in a commercial unit. The *Removal Efficiency* decreased from 85 % to about 40 % with the higher gas flow.

Based on the data presented in Table 8 it can be noted that there is significant variance in results obtained for “the same“ conditions. The error (about 10 %) comes from independent changes in process variables during field tests, like fluctuations of: solution temperature, pH, air and water flow rates. Scattering of the data is also associated with the error of sampling and analysis, and it is typical for such field test conditions.

Further work was proposed for a third field test, to study the stripping cyclone with a new design and to provide experimental data for improved operation. The mobile ASH system for further tests was equipped with two stripping ASH units connected in series.

The third round of field tests took place April 25-May 5, 2003. To secure minimal resistance to the flow of the gas phase, the traditional porous tube was replaced with stainless steel mesh. A tangential air inlet provided more uniform flow of gas through the mesh. Additionally, a two stage stripping arrangement with one absorption stage in a closed gas circuit was examined (see Figure 20, and Figure 21).

At the beginning the 6” ASH served for absorption of HCN since its efficiency and reliability was confirmed during the second series of tests. Later it was replaced with the newly designed 2” ASH unit. The alkaline solution was fed to the cyclone through a conventional Krebs header and a custom-made header allowing feed to the ASH with a lower flow rate but still with an entry velocity of 6 to 7 m/s. The dependence of gas pressure drop vs. linear velocity of the alkaline solution is shown in Figure 22. It can be observed that for the same inlet velocity the pressure drop for the conventional 2’’ Krebs header was ten times greater than for the custom made header with narrow slot.

The alkalinity of the solution in the third tank was adjusted to a value between pH 12.4 to 13.2, and the flow rate of the aqueous phase was changed to within 2 to 5 gal/min. The HCN content in the discharged gas phase was comparable to the level obtained during the second field tests when the 6” ASH was used for absorption. However, better results were obtained for the 2” ASH at the same conditions, i.e. less than 15 ppm at a pH value of 13 and 90 scfm gas flow rate. Moreover, the required alkaline solution flow rate was much smaller. See Figure 23. Recirculation of the gas phase resulted in smaller consumption of caustic solution due to absence of carbon dioxide.

Table 9. Processing conditions and efficiency of HCN stripping in a single 2'' modernized ASH unit using stainless steal mesh tube.

No.	Gas Flow Rate [scfm]	Water Flow Rate [gal/min]	Stripping Temp. [°C]	pH [-]	Initial CN^- Concentr. [ppm]	CN^- Concentr. after 1 pass [ppm]	Actual Q* [-]	Required Q* [-]	Actual Removal [%]	Removal Efficiency [%]
1	40	3.5	20	4.4	371	292	85	213	21	**53**
2	42	3.5	20	3.9	406	329	90	213	19	**45**
3	42	3.5	20	3.9	329	276	90	213	16	**38**
4	45	3.5	20	4.0	390	328	96	213	16	**36**
5	71	3.5	21	4.2	385	244	152	206	37	**50**
6	71	3.5	21	3.0	385	218	152	206	43	**58**
7	77	3.5	21	4.0	380	260	165	206	32	**40**
8	80	3.5	19	3.9	380	291	171	221	23	**30**
9	90	3.5	20	4.1	390	276	192	213	29	**32**
10	90	2.0	21	4.1	385	208	337	206	46	**28**
11	90	5.0	21	4.1	385	296	135	206	23	**35**
12	100	3.5	21	4.0	380	244	214	206	36	**35**

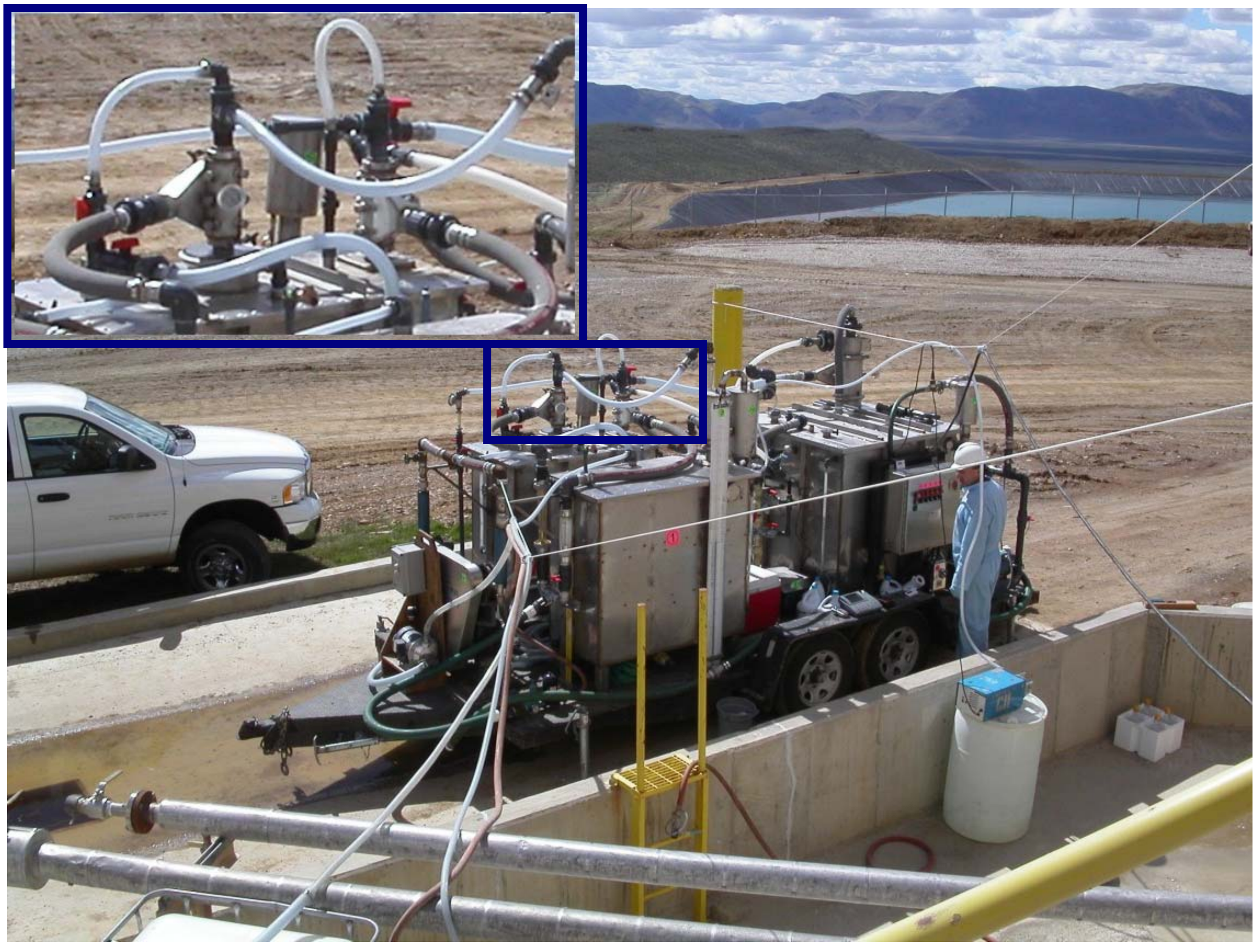


Figure 20. Mobile ASH system with redesigned hydrocyclones and closed air path, installed near CCD circuit at the Newmont Mining Corporation gold cyanidation plant near Midas, Nevada.

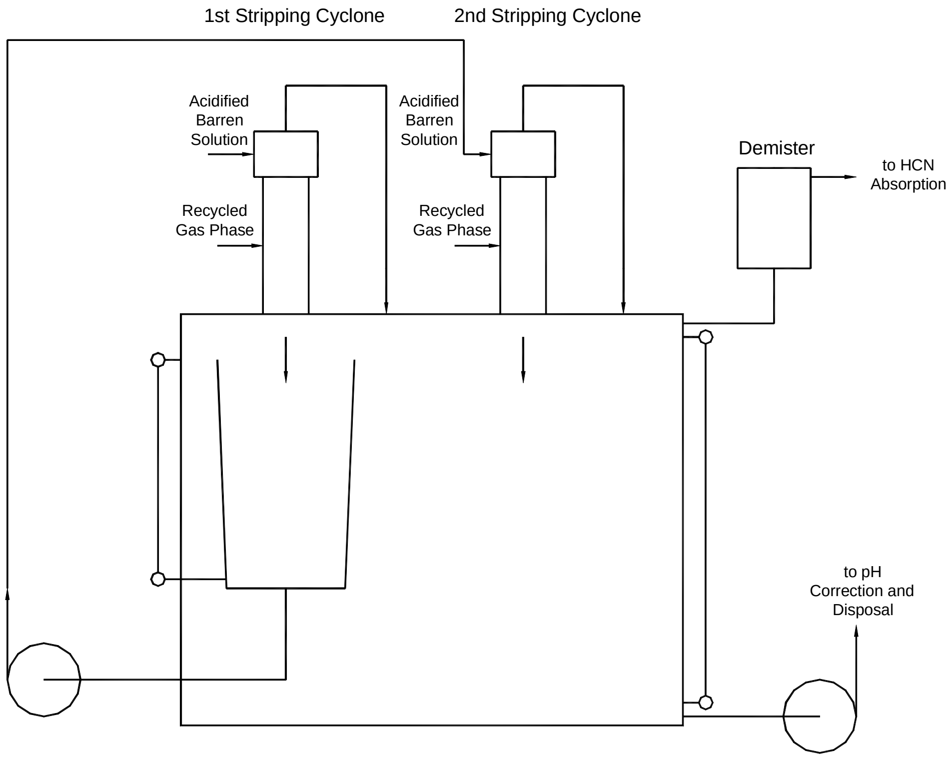


Figure 21. Two stage ASH stripping system installed in tank 2 during third round of field tests in Newmont Gold Mine near Midas.

The HCN stripping efficiency data is shown in Table 9. Stripping tests were performed at a constant barren solution flow rate (3.5 gpm), pH = 4.0 ± 0.3 and variable air flow rate from 60 to 100 scfm. The pH was adjusted using sulphuric acid. The data indicate that the maximum *Actual Removal* reached 46 %. For larger Q* (gas phase/liquid phase volumetric ratio) the A*ctual Removal* of HCN from the barren solution was better. Nevertheless, increase of the A*ctual Removal* with increased air flow rate from 70 to 100 was minimal (a few percent) which does not justify the high air flow rate in the present design of the stripping ASH. The stripping efficiency has not been optimized for the new sparger, therefore, better performance of the new type of ASH can be expected.

Process efficiency, shown in Figure 24, indicates that besides Q* other processing parameters have a pronounced impact when steel mesh is used as the sparger. For example, with respect to the barren solution flow rate, both 2 gpm and 5 gpm showed lower performance than 3.5 gpm. Thus the previously recommended inlet velocity 6 – 7 m/s, corresponding to 3.5 gpm flow rate, has been confirmed and is important for design purposes. Another set of experimental data is shown in Figure 25. The dependence of removal efficiency on the air flow rate is shown, and similar to Figure 24 the efficiency oscillates around 40 %. Due to more stable pH (3.9 to 4.2) the efficiency fluctuations also less. From Figure 24 and Figure 25 it can also be noted that the removal efficiency is adverse to actual removal when compared for experiments of different Q*'s.

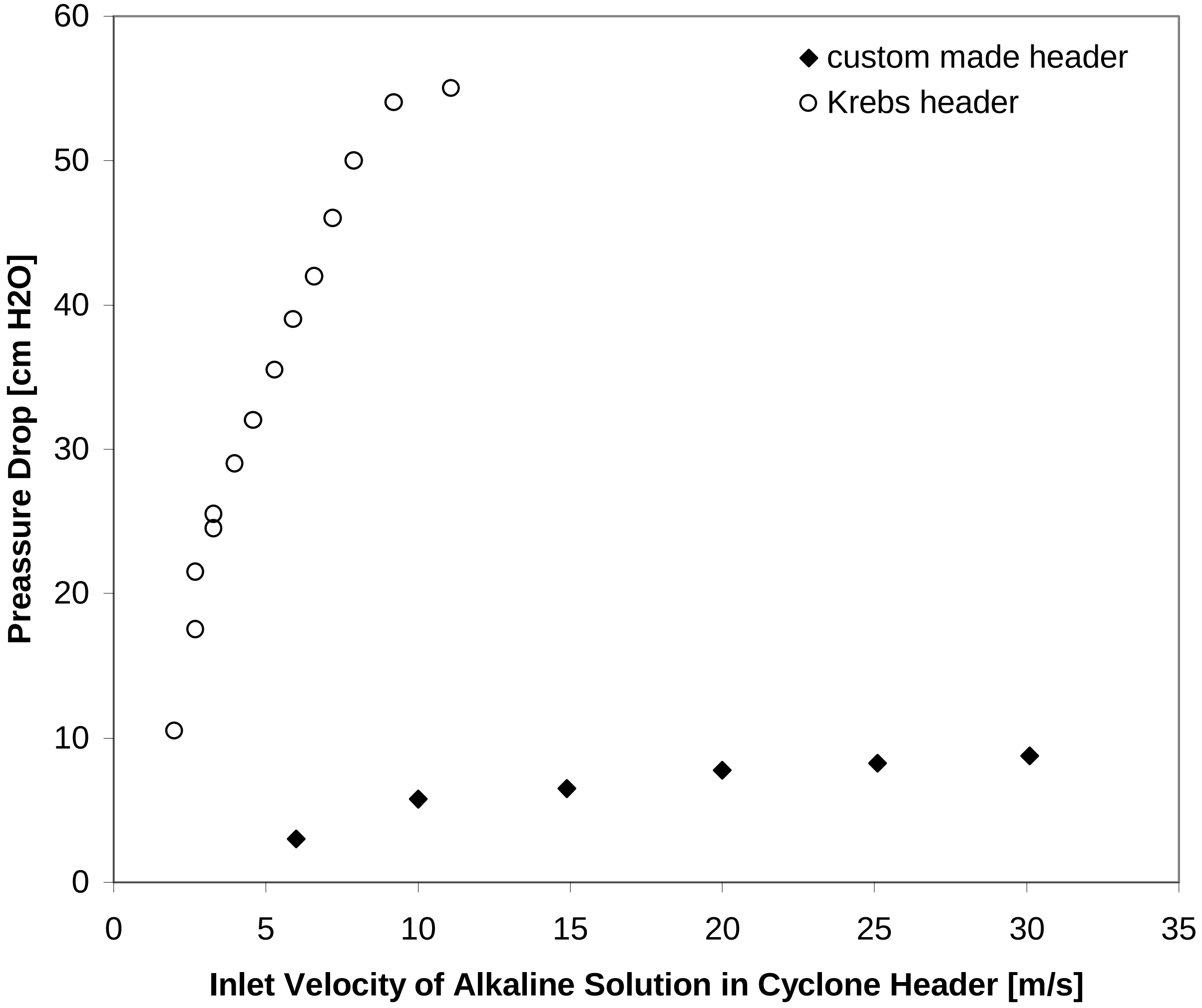


Figure 22. Gas pressure drop across the cyclone (equipped with stainless steel mesh tube) vs. inlet velocity of alkaline solution in 2'' Krebs (1.54 cm^2 inlet opening cross section, 90 scfm of air flow) and 2'' custom made header (0.32 cm^2 inlet opening cross section; 76 scfm).

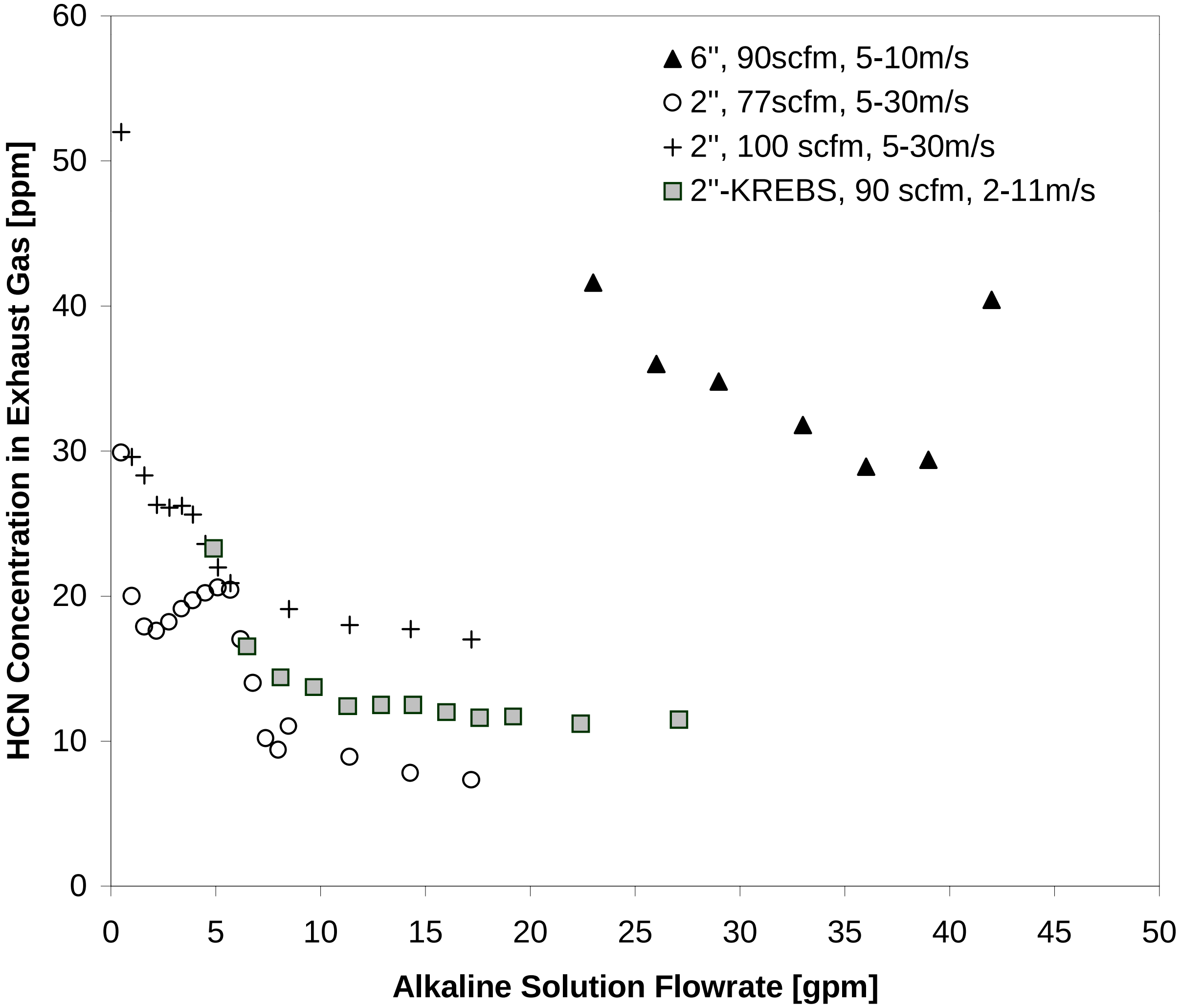


Figure 23. HCN concentration in exhaust gas vs. flow rate of alkaline solution (temp. 15.5-25.0 °C and pH 12.5-13.4 for 2" cyclone, temp. 7.5-9.1 °C and pH 13.3-13.4 for 6" cyclone).

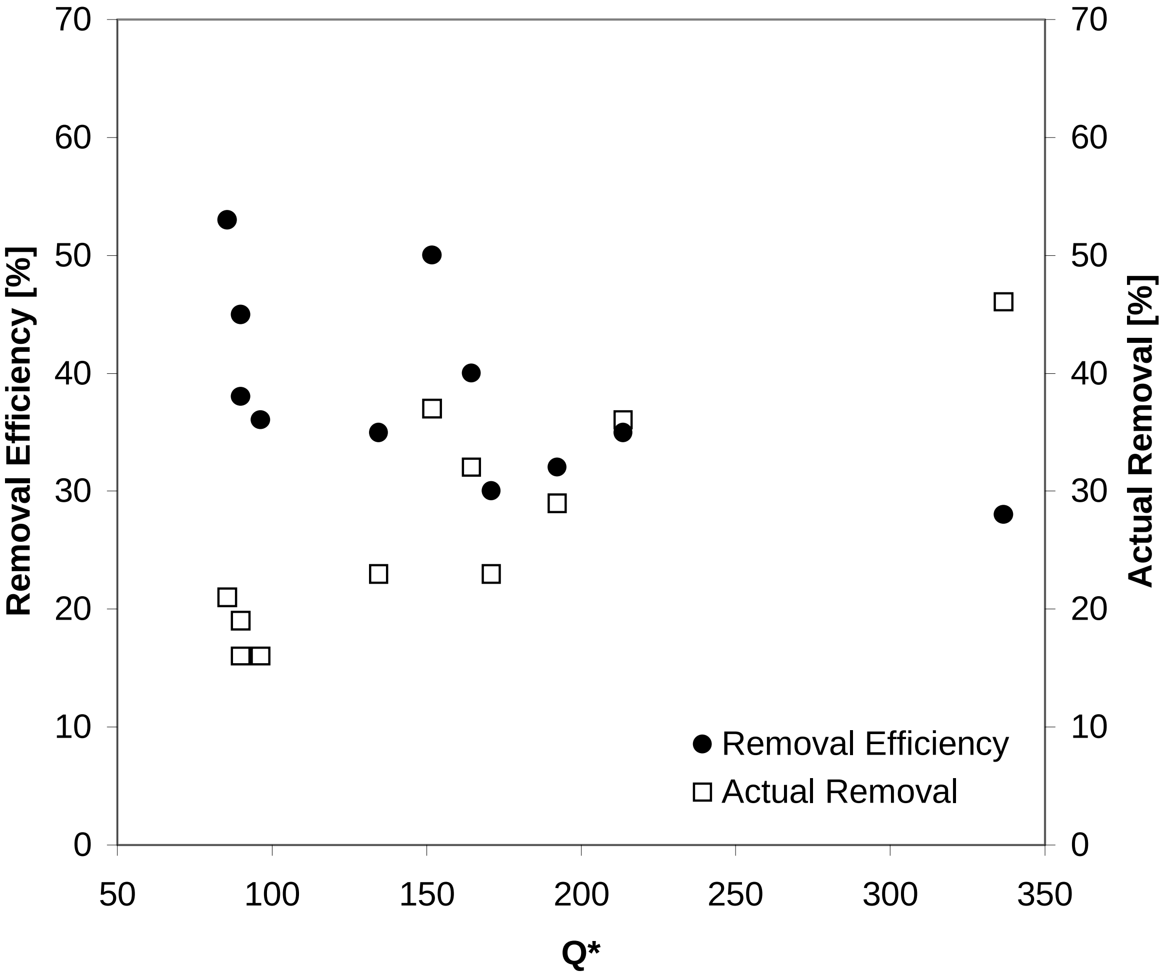


Figure 24. HCN removal efficiency and actual removal vs. air/liquid ratio (air flow. 40-100 scfm, stripped solution flow rate 2-5 gpm, stripping temperature 19-22 °C, pH 3.9-4.4).

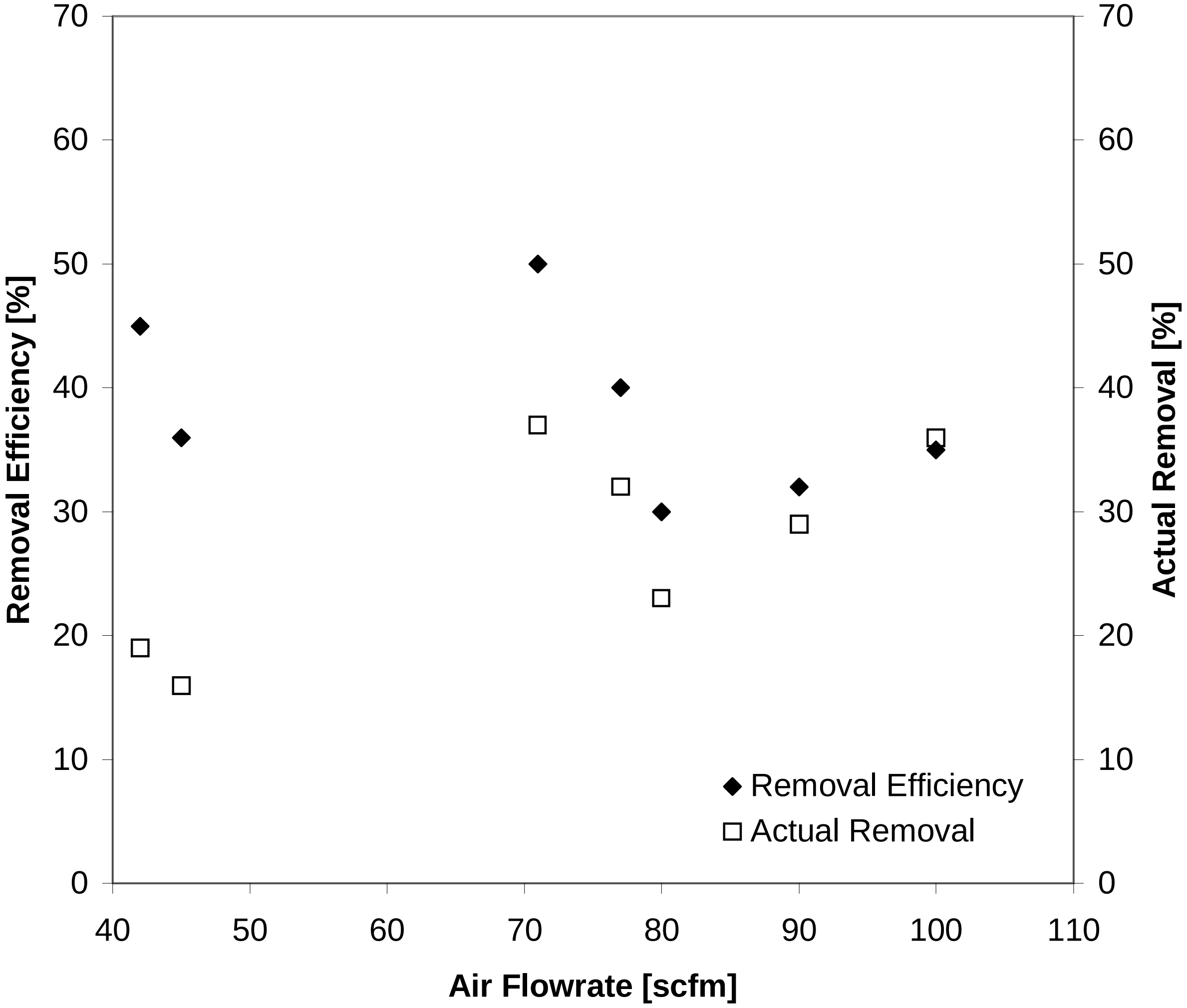


Figure 25. HCN removal efficiency and actual removal vs. air flow rate (stripped sol. flow. 3.5 gpm, temp. 19-21 °C, pH 3.9-4.2).

The two stage stripping arrangement, shown in Figure 20, was tested with 6" absorbing ASH unit since only two 2"ASH units were remodeled. The combined performance of the two-inch ASH units (see experiments No. 2 and 3 in Table 9) was slightly less efficient than twice the efficiency of a single ASH unit. Nevertheless, two different headers were available thus not allowing for optimal stripping conditions in both cyclones at the same time (different inlet feed velocity due to different opening, necessary for other studies). However, the two step stripping module operated without any problem using both one pass and recycled mode of operation for the gas phase.

8.2.3. Investigation of Plugging

Fouling of the porous tube was one of the most troublesome issue faced during experiments with mobile unit. Although plugging of the porous PE tubes was not significant for ASH stripping with the synthetic cyanide solution, made with tap water, plugging became severe during field tests.

The rate of plugging was observed to be different for the re-absorption (R) tubes as compared with the stripping (S) ones. The pressure drop on the R tube increased steadily, whereas the plugging of the S tube was very slow at the beginning, but more rapid at the end.

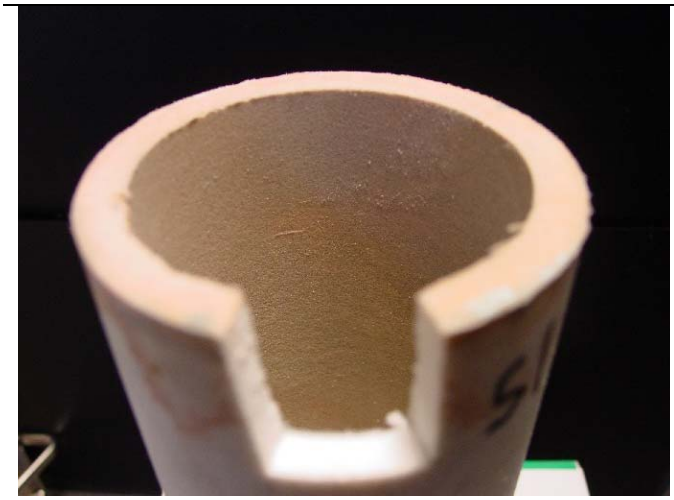
Initially it was suspected that the mechanism of plugging of the S tubes was physical; possibly a filtering of crystals or amorphous sediments. The smaller the pore size became, due to plugging, the faster additional material was deposited. Accumulation of deposits within the R tubes was attributed to the formation of calcium carbonate. Calcium carbonate may be formed when CO_2 contained in the air passes into the alkaline solution.

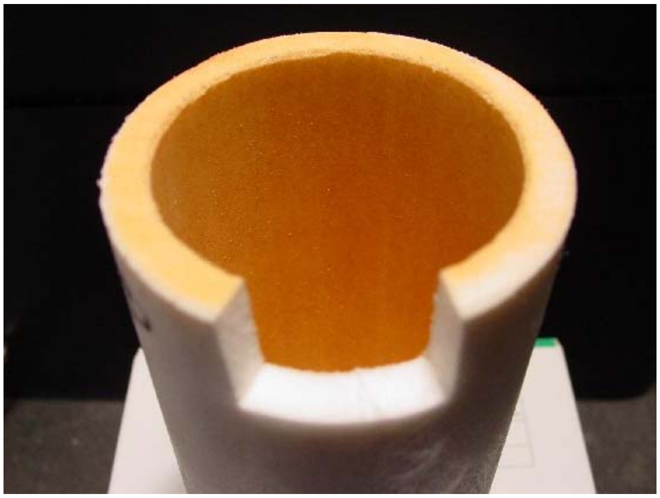
Samples of different porous tubes used during experiments were collected (see Table 10) and analyzed to determine the chemical nature of the sediments. Tube samples for analysis were cut from one side of each porous tube. The size of the porous tube samples was reduced and the cuttings were leached with deionized water and hydrochloric acid. 20 grams of the material was submerged in 200 ml of 10 % HCl solution or 200 ml deionized water for 24 hours. 100 ml of clear supernatant were submitted for the ICP analysis. The chemical analysis of the plugging solids is provided in Table 11. Since the Ca/S ratio in the sample from the stripping tubes is close to one, it can be inferred that the compound is calcium sulfate: Also, the mill solution was very high in calcium, from the calcium hydroxide used to raise the pH to 11, and the fact that this solution is recirculated in the circuit and from the tailings pond. The sulfate came from the sulfuric acid used for acidification. For ASH experiments with hydrochloric acid rather than sulfuric acid, plugging occurred, but took a longer time. Hydrochloric acid would likely not be economical for acidification purposes and build-up of chloride in the process water might be of concern due to a point of corrosion and environmental considerations.

Reabsorption tubes had very high Ca/S ratios (about 25:1, 5:1 and 2.3:1). The variation in ratios was due to the type of water used in the reabsorption circuit, and different processes performed in the absorption tank. For example, the first set of tube R1 (see Table 10) served only for absorption and alkaline chlorination thus a high Ca:S ratio is not surprising. The second set of tubes (R2) were used also for INCO SO_2/Air tests (sodium metabisulfite was present in the solution), so a decreased Ca:S ratio could be expected. The last set of examined tubes (R3) served only during the first field tests with process water, containing sulfates, and were used for preparation of the chemicals, so the Ca:S ratio is relatively small. During next field test tap water was available for preparation of the chemicals, and the air path was closed, so plugging in the absorption circuit was not noticeable. The other thing is that in the case of absorption even if there is a deposit it would not be so critical, since both calcium carbonate and/or calcium hydroxide can be readily dissolved with an acid wash. Likely it would be more difficult to prevent the formation or to remove gypsum (calcium sulfate) from the stripping tubes.

Backscattered electron images (BEI), see Figure 26, and x-ray energy dispersive (EDS) spectra from an examination of the deposits on selected S and R ASH tubes was done by Newmont Metallurgical Services. EDS analysis indicated that solids found on S tubes were gypsum needles. R3-1 tubes contained only mineral fines, such as quartz, muscovite, chalcopryite etc. An EDS analysis obtained during low-magnification scanning showed mostly Si, indicating mostly quartz. The R3-2 material was mostly calcite, with minor amounts of intermixed gypsum.

Table 10. Porous tubes examined for chemical composition of the deposited material.

Sample	Origin/Comments
	S1: Stripping tube. Mainly used in laboratory batch tests (lasting about one half of a year at the U/U), replaced by S2 after working about additional 4-5 hours field test in Midas. Only H_2SO_4 was used with it. Tube was replaced because of plugging during field test. Newmont Research notes: “The S-1 material was practically all gypsum needles. These are readily visible with a stereomicroscope.”

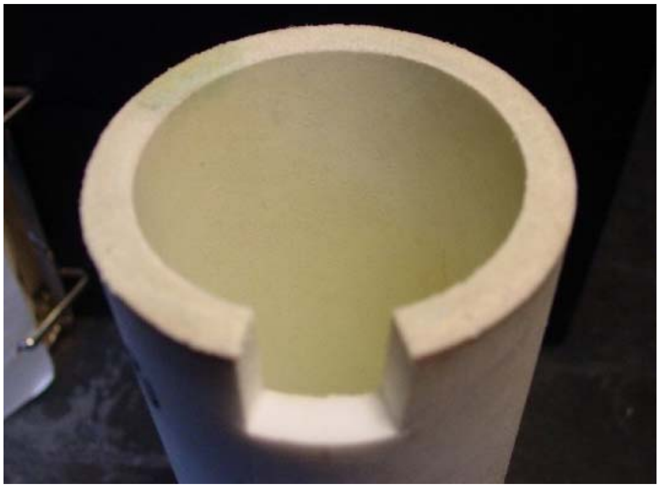


S2: Stripping tube.

Used only in field tests in Midas. Run 9-10 hours first with $H_2SO_4$and at the pH of 7~3, then about 3 hours with HCl at the pH of 6~7.

R1a:Re-absorption tube.

One from the first set of reabsorption tubes, used in batch tests at the U/U. for reabsorbtion, at the pH of 12.5~13 with NaOH addition; lasting about 3-4 months before replacement (because of plugging). Tube was mounted on the tank, where degradation of cyanides with sodium hypochlorite was performed.



R1b: Re-absorption tube.

One from the first set of reabsorption tubes, used in batch tests at the U/U for re-absorbtion, at the pH of 12.5~13 with NaOH addition; lasting about 3-4 months before replacement (because of plugging). ASH equipped with such tube served as contactor during degradation of cyanides with sodium hypochlorite.

R2a: Re-absorption tube.

One from the second set of re-absorption tubes, mainly used in batch tests at the U/U for re-absorption, at the pH of 12.5~13 with NaOH addition and cyanide degradation using INCO method (a few runs). The ASH served also as contactor during degradation of cyanides with sodium hypochlorite. Replaced after running about one-hour preliminary field test in Midas (because of plugging), lasting about 3 months.

R2b: Re-absorption tube.

One from the second set of re-absorption tubes, mainly used in batch tests at the U/U for re-absorption, at the pH of 12.5~13 with NaOH addition and cyanide degradation using INCO method (a few runs). The ASH served also as contactor during degradation of cyanides with sodium hypochlorite. Replaced after running about one-hour preliminary field test in Midas (because of plugging), lasting about 3 months.

R3a: Re-absorption tube.

One from the third set re-absorption tubes, used in field tests only, at pH 12~13 with NaOH (in process water), lasted about 3 hours, was used with the S2 porous tube stripping (pH 6~7 with HCl). Re-absorption tank was filled with process water through this porous tube.

Newmont Research notes:
“R3-1 contained only mineral fines, such as quartz, muscovite, chalcopryite etc. An EDS analysis obtained during low-magnification scanning showed
mostly Si, indicating mostly quartz”.

R3b: Re-absorption tube.

Another tube from the third set used for re-absorption in field tests only, at pH 12~13 with NaOH (in process water), lasted about 10 hours with the S2 porous tube for stripping (pH 3~7 with H_2SO_4).

Newmont Research notes:
"R3-2 material was mostly calcite, with minor intermixed gypsum. I double-checked calcite in our lab by adding 10% HCl, which yielded CO_2 bubbles. This sample appeared to contain the most foreign material."

Table 11. Results of chemical analysis of deposit leached form porous tubes.

Sample Number	Reported Sample Number	Corresponding Porous Tube	Main Chemical Composition, mg/L					Ca/S Atomic Ratio	Leaching Reagent
			Ca	S	Na	Fe	Zn		
01	1001358-001	R1a	12.4	6.8	9.64	0	0.05	1.46	Deionized Water
02	1001358-002	R1b	15.1	6.1	8.1	0	0.05	1.98	
03	1001358-003	R2a	60	48.8	25.7	0	0.17	0.98	
04	1001358-004	R2b	67.2	60.5	27.4	0	0.15	0.89	
05	1001358-005	R3a	28.8	22	24.9	0	0.16	1.05	
06	1001358-006	R3b	28.6	18.6	17.1	0	0.49	1.23	
07	1001358-007	S1	459	326	20.2	0	2.64	1.13	
08	1001358-008	S2	55	39.7	6.32	0	0.12	1.11	
09	1001358-009	R1a	368	12.3	12.4	9.8	0.96	23.93	10 % HCl
10	1001358-010	R1b	344	10.7	8.12	8.3	1.31	25.72	
11	1001358-011	R2a	349	47.8	23	14.1	3.83	5.84	
12	1001358-012	R2b	424	64.3	34.3	26.5	4.35	5.28	
13	1001358-013	R3a	47.6	17.1	16.3	2.7	1.89	2.23	
14	1001358-014	R3b	44.5	15.4	13.4	2.1	1.91	2.31	
15	1001358-015	S1	368	281	17.1	17.5	4.74	1.05	
16	1001358-016	S2	51.1	35.2	5.7	9.8	2.47	1.16	

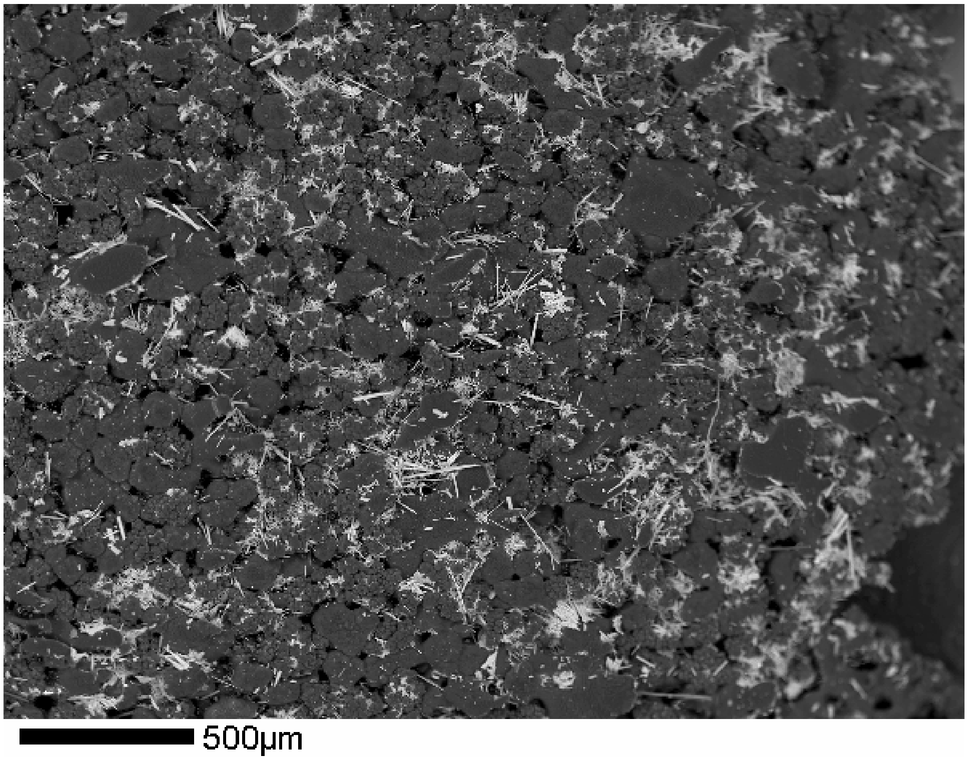


Figure 26. Backscattered electron image of inner wall of S1 stripping tube showing gypsum crystals deposited on internal wall of porous tube.

The following factors would have contributed to the fouling of the porous tubes:

Initial mineral characteristics of barren solution that utilizes lime for pH control.

Addition of sulfate anions via addition of sulfuric acid for pH reduction.

Addition of CO_2 (contained in air) as air is passed to the alkaline solution.

Preparation of caustic using recycled water containing fines.

Washing of tubes with process water containing fines.

As a recommendation it was suggested that water with minimum suspended solids (tap or deionized water) should be used to prepare dilute solutions of caustic/acid. Reduction of plugging due to mineral deposits can be achieved by the use of scale inhibitors that prevent the formation of gypsum and calcite. Feed points should be prior to the S tubes and the R tubes. The use of dilute muriatic acid could be applied for removing calcium carbonate scale deposits during washing procedures.

The barren cyanide solution contained several grams per liter of dissolved salts. The mill experiences, therefore, severe scaling problems in several areas. It is not surprising, that the stripping ASH underwent rapid plugging as well. The plugging rate of the stripping ASH porous tube increased when the air flow rate was changed from 60 to 120 scfm. Such dependence may indicate that the mechanism of plugging is evaporation of water at the internal surface of the porous tube. Plugging happened despite removal of all particles $<1\,\mu m$ by bag filtration. Plugging was diminished when hydrochloric acid was used for acidification, scale-control chemicals were added to the barren solution, and mist of deionized water droplets was introduced with the gas phase to the PE porous tube. Simultaneous application of hydrochloric acid and descalant extended the lifetime of a porous tube for over 8 hours. However, particularly effective was injection of 1 gal/hr of deionized water to the gas stream. To investigate this further, permeability measurements for new and plugged porous tubes were performed. Pressure drops during air flow (500 L/hr) through the wall of porous tube in different locations were measured and permeabilities were calculated according to Equation (22):

$$K_p = \frac{\mu \cdot u \cdot L}{\Delta P} \quad [\mu m^2] \tag{22}$$

where μ = air viscosity [Pa·s]
u = linear air velocity [μm/s]
L = bed thickness [μm]
ΔP = pressure drop [Pa]

In Figure 27 and Figure 28 permeability of fresh porous material and porous tube used during the field tests (when mist of the distilled water was applied to the gas stream) is shown. As is shown in the plots, when humidified air reached the surface of porous material no deposits were formed, and no decrease in permeability was measured. Though it is also clear that gas phase was not evenly distributed in traditional design of the cyclone housing. Therefore it was decided that the new stripping ASH would be equipped with spraying nozzles and tangential inlet for the gas phase.

An earlier investigation at the University of Utah indicated that slow plugging took place during stripping of perchloroethylene from underground water (in which only a small quantity of fine particles was present). During earlier applications of the ASH for flotation much less air was used (lower Q*) therefore the ASH was more resistant to plugging.

To evaluate the rate of deposition of scale on the wire mesh screen tube, which served as a sparger, the change in mass of the screen was measured before and after completion of the experiments.

It should be noted that the 2" ASH unit which underwent severe plugging in 2 to 10 hours when PE porous tube was used as the sparger, the wire mesh tube functioned without any pressure drop increase through the entire week of tests, see Figure 29. At the end of tests, after 65 hours of operation, the stainless steel mesh was scale free. Thus antiscalant addition was not necessary. The pressure drop in the cyclone for the gas phase was 0.5 to 1 inches of H_2O. The required pumping pressure for the alkaline solution was 6-7 psi, which corresponds to (or is less than) the pumping head necessary for absorbing packed towers in the AVR system.

Some scale precipitation is noticeable in photographs shown in Figure 29 and Figure 30. These results correspond to a mass gain of the mesh stripping insert equal to 1.5 g. It seams that application of the mesh screens could extend operational life of the unit to some reasonable period, acceptable by industry.

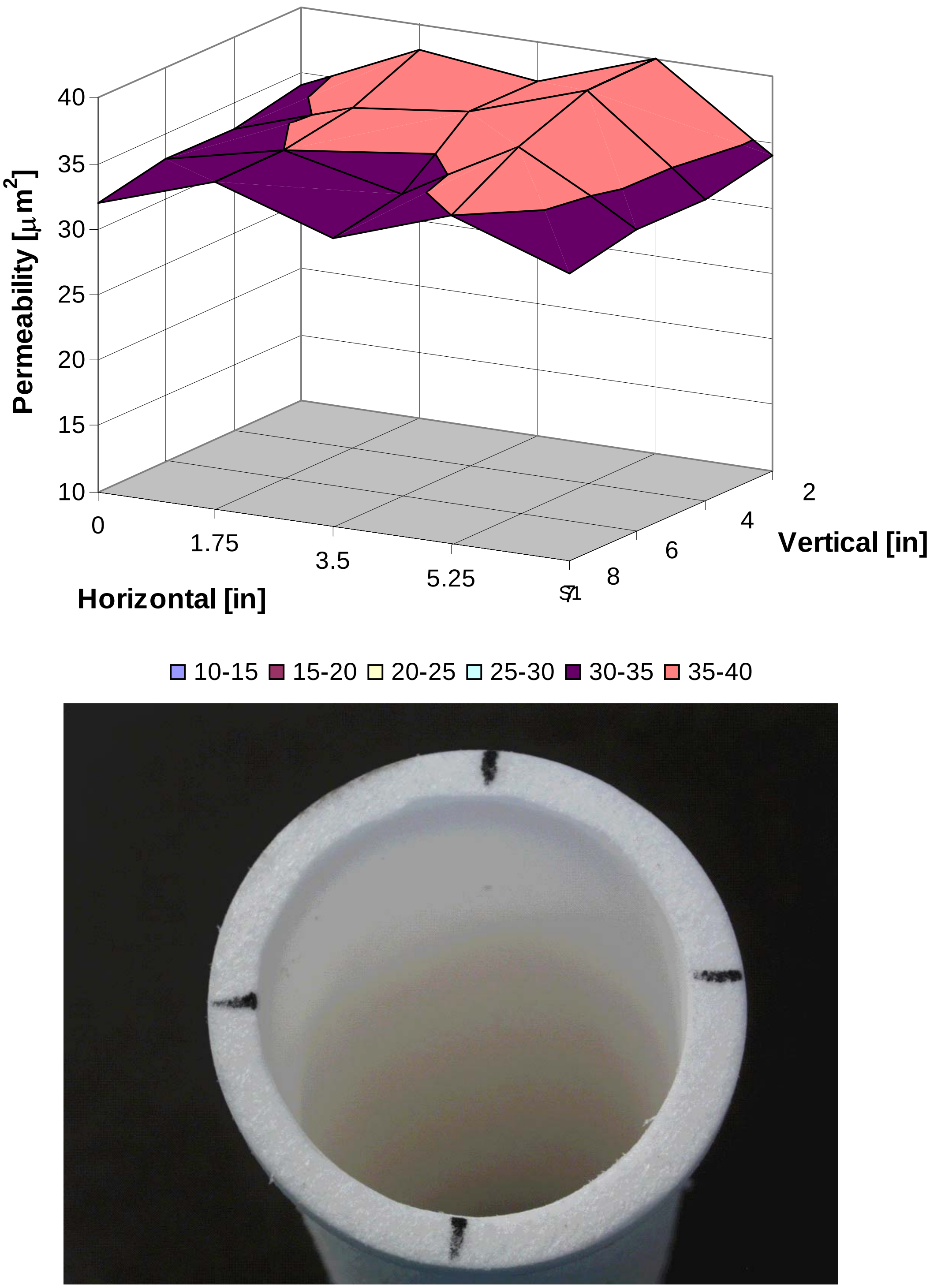


Figure 27. Permeability plot of new porous tube along with a view of the tube.

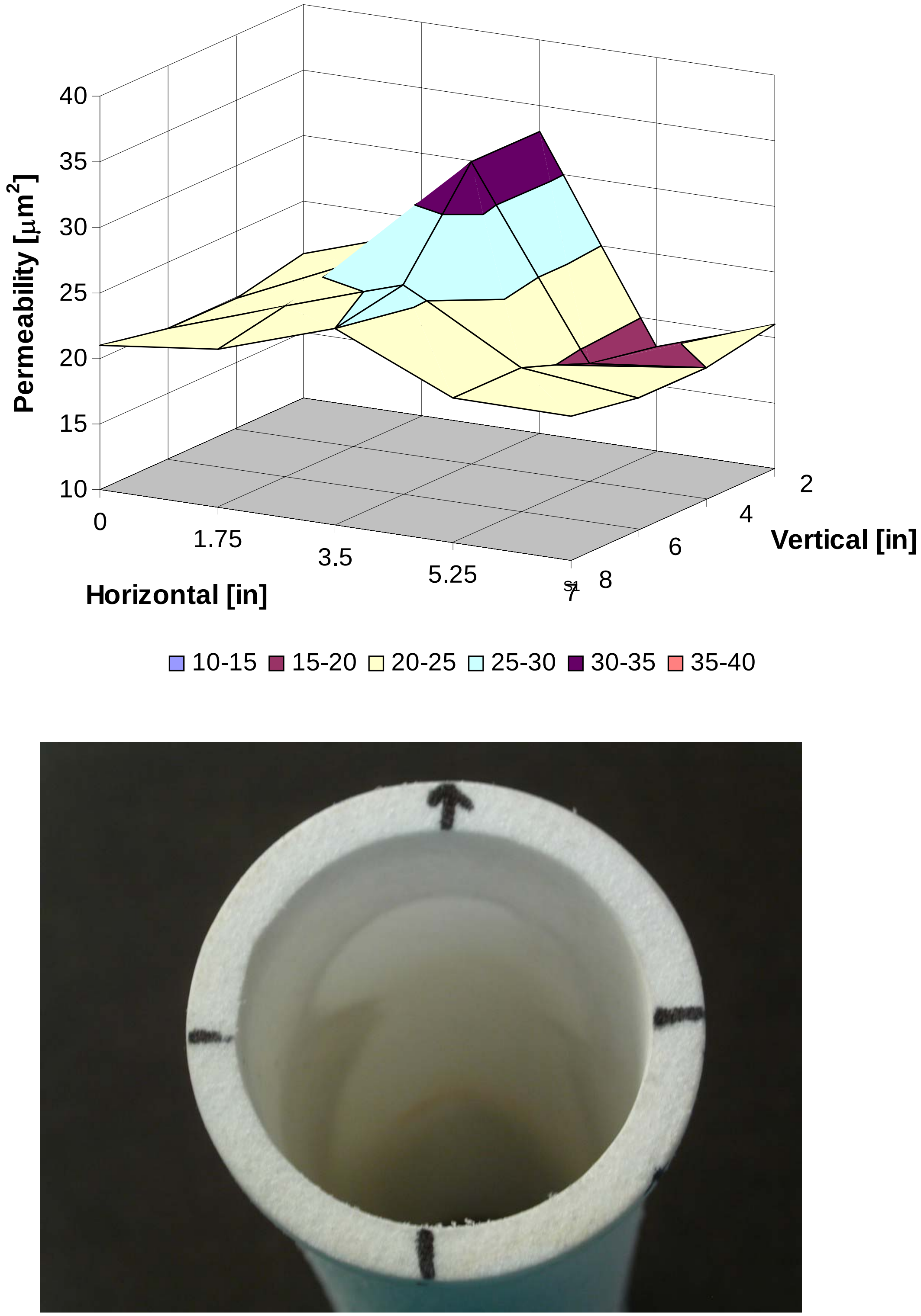


Figure 28. Permeability plot of porous tube used during the field test with humidified air, along with the view of the tube.

Figure 29. View of stainless steel mesh tube used as spargers in newly designed ASH units after field tests: left – after absorption; right – after stripping.

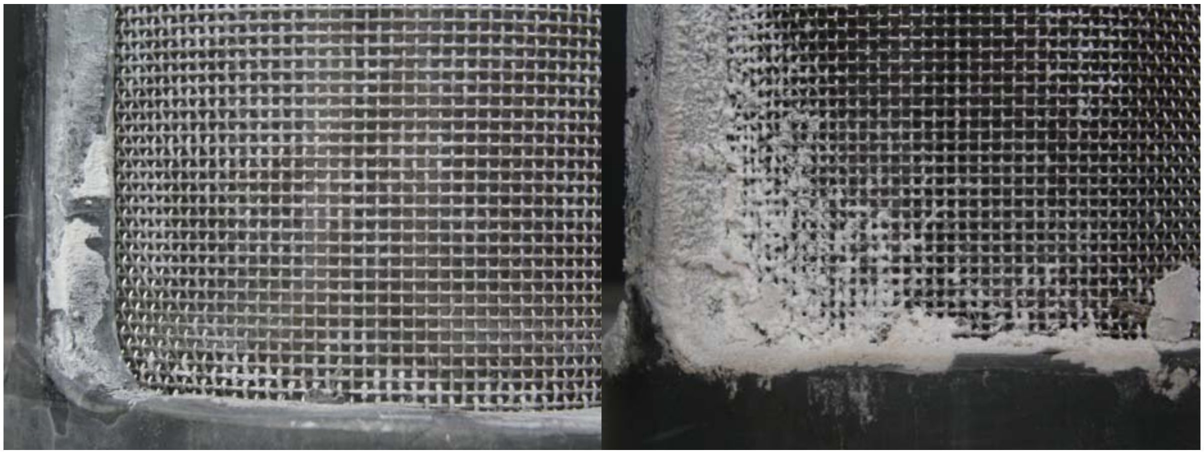


Figure 30. Extent of scale formation during absorption (left) and stripping (right).

8.2.4. Mass Transfer Coefficient

The Air-Sparged Hydrocyclone utilizes high liquid shearing forces to produce small gas bubbles and hence high interfacial area coupled with centrifugal forces to enhance the mass transfer coefficient and promote subsequent phase separation. These benefits are achieved by tangential inlet of the liquid into a porous tube through which the gas flows. The liquid forms a spinning layer on the inside of the tube wall. Gas passes through this layer as fine bubbles and, due to the centrifugal forces, forms a central core. The enhanced acceleration field causes an increase in the mass transfer coefficient.

The well-trodden two-film theory, which is widely employed to represent interfacial mass transfer, states that the total resistance for liquid-to-gas mass transfer is equivalent to the sum of resistances contributed by the liquid and gas stagnant interfacial films [21]:

$$\frac{1}{K_L a} = \frac{1}{k_L a} + \frac{1}{H_C k_G a} \tag{23}$$

where, K_L = overall liquid mass transfer coefficient,
a = specific surface area,
k_L = liquid side mass transfer coefficient,
k_G = gas side mass transfer coefficient,

or mass transfer coefficient (K_La) can be calculated using the following relationship [22]:

$$K_L a = \frac{Q_L}{H_t A}\left(\frac{S}{S-1}\right)\ln\left(\frac{1}{S}+\left(1-\frac{1}{S}\right)\left(\frac{C_{LI}}{C_{LE}}\right)\right) \ [\mathrm{min}^{-1}] \tag{24}$$

where, Q_L = liquid flow rate,
H_t = height of air stripping tower,
S = stripping factor,
C_{LI} = influent cyanide concentration,
C_{LE} = effluent cyanide concentration,

And the stripping factor S can be calculated from the equation:

$$S = \frac{Q_G}{Q_L} H_c \tag{25}$$

where, Q_G = gas flow rate

Strictly, equation (24) applies to a pure countercurrent flow situation whereas flow in the ASH is more complex involving cross and counter flow. However, even in a packed column there are conditions at high Q_G/Q_L where some recirculation of gas is likely and yet that concept is still applied for simplicity [23]. Calculations of K_La values is a good basis to compare ASH performance with the performance of a packed column as it takes into account both the height requirement and the liquid flux capabilities of the two devices. The K_La data are based on the countercurrent plug flow approximation for water and gas flow within the ASH and the packed column. However the flow patterns of gas and liquid within the ASH are clearly more complex than for countercurrent plug flow. There will be some initial cross flow of gas through the liquid, some co-current flow as bubbles begin to travel with the liquid and some countercurrent flow as gas and liquid leave from opposite ends of the porous tube. The effective mean mass transfer driving force will therefore be less than that for countercurrent plug flow. Thus true K_La values for the ASH will be higher than those calculated from equation (24), and (25) [23].

The calculations of the K_La for the ASH are presented in Table 12. Based on this data it can be concluded that mass transfer coefficient decreases with an increase in gas to liquid ratio. Better mass transfer coefficients were obtained for the PE porous tube than for the mesh screen tube. Also an increase in tube height (2 sections of the cyclone) did not improve mass exchange but cut efficiency in half. These results suggest that the loss of velocity caused by friction as the liquid stream goes down the porous tube makes mass transfer ineffective, and there is no need to use cyclone sections longer than 30 cm. For example it was found in the literature [24] that K_La values for a 89 mm x 1.85 m packed column used for MTBE removal, were in the range 0.166–0.0267 min^{-1}, which is from one to two orders of magnitude worse than for the ASH.

Table 12. Stripping factors and values of mass transfer coefficient for HCN stripping experiments.

No.	Q* [-]	Water Flow Rate [gal/min]	Stripping Temp. [°C]	pH [-]	Initial CN^- Concentr. [ppm]	S	K_La [min^{-1}]	Cyclone Height [cm]	Sparging material	Treated solution
1	75	7.5	30	3	412	0.41	3.52	30	PE porous tube	synthetic
2	112	5.0	30	5	194	0.62	1.65	30	PE porous tube	synthetic
3	128	3.5	32	5	364	0.75	0.88	30	PE porous tube	barren solution
4	128	3.5	18	3	423	0.47	0.42	60	PE porous tube	barren solution
5	152	3.5	21	4	385	0.61	0.46	30	SS mesh	barren solution
6	152	3.5	21	3	385	0.61	0.65	30	SS mesh	barren solution
7	192	3.5	15	4	395	0.63	0.83	30	PE porous tube	barren solution
8	256	3.5	15	4	395	0.83	0.65	30	PE porous tube	barren solution
9	337	2.0	21	4	385	1.36	0.25	30	PE porous tube	barren solution

9. Comparison of ASH to Packed Towers – Economic Analysis

A number of plants for the recovery of cyanide from precious metal processing solutions have been built and operated over the past years using the AVR (Acidification-Volatilization-Recovery) technology. Elbow Creek (a contributing sponsor of the ASH/CN project) has produced capital and operating cost estimates for ASH/CN and AVR. Because these cost models for AVR have been used in conjunction with the design and construction of several AVR plants worldwide, it is felt that the preliminary cost estimates are of a good order of accuracy. The cost model for the ASH/CN process is based on the AVR model, but has considerably more potential for variation, since the ASH/CN process is still in the development stage, and since critical engineering value analysis has not been carried out on the overall process and preliminary design.

There are two areas of interest in the economic analysis of cyanide recovery. The first area is the traditional economic analysis which includes the direct operating cost for the process, which can be expressed in terms of dollars per pound of recovered NaCN suitable for direct reuse in the system, and the estimated capital costs in order to provide an overall economic analysis. The second area of economic interest is applicable for plants such as Midas that must destroy all or part of the cyanide in their process discharge stream in order to meet environmental regulations. Recovery of cyanide would reduce or eliminate these costs. The percentage recovery of cyanide using acidification depends on the pH reduction in the treated solution and the related conversion of complexed cyanides to HCN and the efficiency of stripping of the HCN. In almost all cases where cyanide destruction is required, the optimum operating conditions for HCN removal would be a function of the increase in cost for increased HCN recovery and the decrease in cost for destruction of the remaining cyanide. The price of sodium cyanide has varied significantly over the past ten years but has generally varied between US$0.55 and 0.65 per pound for bulk deliveries.

Early pilot plant work with the ASH unit showed problems not only with plugging, as noted above, but also with the pressure drop across the system. Initial capital and operating cost estimates for the ASH system were developed using the measured system pressure drop of about 55 inches H_2O (2 psi). The base case system for comparison, packed columns, has a system pressure drop of 11.5 inches H_2O (0.4 psi). Both the capital cost for the ASH system (primarily for blowers in place of fans) and the operating costs (increased horsepower for blowers for the ASH unit) were significantly higher than the cost for packed columns.

For the second round of pilot tests at Midas the polyethylene porous tube in the absorption cyclone was replaced, as discussed above, with a wire mesh tube that both eliminated the plugging problem and reduced the pressure drop across that cyclone to about 1 inch H_2O. This, and a few other changes reduced the system pressure drop for the second field test to about 19 inches H_2O before plugging in the stripping cyclone began to build up. The economics for the Midas circuit shown below have been estimated using this pressure drop, and still indicate a higher capital and operating cost of ASH versus packed columns – primarily due to the higher pressure drop with the ASH system.

With the success of the mesh tube in the absorption circuit, a similar tube was installed in the stripping circuit, for the third Midas run. Calculations and earlier test data indicate that the system pressure drop with this modification would be in the range of 8 inches H_2O – comparable to the 12 inches H_2O of the AVR/packed column system. Since this pressure drop is the reasonable goal of the next pilot plant cycle, economics have been run for Midas using this reduced ASH/CN value as a possible lower limit. Both capital and operating costs for the ASH/CN system under these conditions are similar to those of the AVR system, within the accuracy of the estimate.

The proposed cyanide recovery process for Midas calls for acidification of the barren solution to recover cyanide, with this cyanide-depleted solution used as wash solution for the CCD circuit. This would reduce the concentration of cyanide in the feed to the Inco SO_2/Air process from about 325 mg/L WAD cyanide to about 21 mg/L, markedly reducing the cyanide destruction costs for this circuit.

These calculations produced the following parameters:

- 367 mg/L WAD cyanide added to leach circuit
- 330 mg/L WAD cyanide exiting leach circuit in pulp
- 325 gpm of pregnant solution fed to Merrill Crowe and cyanide recovery circuits
- 202 mg/L WAD cyanide in CCD pregnant solution
- Final tailings: 42% solids at 21 mg/L WAD cyanide
- Overall cyanide recovery 94% (between CCD and cyanide recovery circuits)

- 490,000 lb. per year NaCN recovered (approximate)

The economic model run with the above input data is presented in Table 13. It is evident that cyanide recovery is not economic under these conditions. However at higher concentrations of cyanide in the feed recovery should be considered, since capital and operating costs are unchanged. Analysis of the cost of cyanide recovery for different concentration in the feed is presented in Figure 31. When the cyanide concentration in the feed increases to around 800 ppm, the recovered NaCN cost goes down to about $0.40/lb. With increased recovery there is more savings on destruction side, which was not included in the above calculations.

Table 13. Economic model for cyanide recovery at Midas Gold Mine using Packed Columns and ASH technology.

	Packed Columns	ASH Technology
Capital Cost	$0.76 million	$0.88 million
Operating Cost, per year	$0.43 million	$0.46 million
Recovered NaCN value/year	$0.32 million	$0.32 million
Recovered NaCN cost	$0.89/lb.	$0.95/lb

The cost of operating the Midas cyanide destruction circuit with its current 360 mg/L WAD cyanide feed concentration was estimated based on the following parameters:

- 276,000 tons per year ore exiting the leach circuit (based on 2002 published Newmont data)
- 42% solids pulp exiting leach circuit
- 2.1 lb. NaCN per ton ore added to leach circuit
- 90% of cyanide added to leach circuit reports to the leach tails (An estimated 10% of the cyanide is consumed in the leach circuit.)
- CCD wash ratio 1.5 tons water per ton solids
- 65% thickener underflow density
- 95% recovery of WAD cyanide in cyanide recovery plant
- Pressure drop across the entire AVR circuit: 11.5 inches WG (0.4 psid)
- Pressure drop across the entire ASH/CN circuit: 8 inches WG (0.3 psid)
- Reagent consumption of 6 lb/ton of ammonium bisulfite and 0.41 lb/t of copper sulphate.

Power consumption was estimated at 80% utilization of the 150 installed horsepower agitators for the circuit. Discussion with engineers familiar with the Inco SO_2/Air cyanide destruction process indicated that reducing the cyanide concentration in the feed to the circuit would reduce the amount of ABS required almost linearly, and the copper sulfate requirement by a large amount. Reducing the concentration to a level of 40 mg/L or less would enable the power consumption to be reduced by half. Using these parameters it was estimated that reducing the concentration of cyanide in the destruction circuit feed to 21 mg/L of WAD cyanide would reduce the operating cost from about \$0.71/t slurry to about \$0.49/t slurry, for an annual savings of \$132,000 per year. The above is based on general information about the Inco SO_2/Air process, and is not based on any testwork at the Midas operation. Applying this value to the previous comparison, results in the following:

Table 14. Economic model for cyanide recovery in Midas Gold Mine using AVR and ASH technology taking into account savings gained on cyanide destruction.

	Packed Columns	ASH Technology
Pounds NaCN recovered per year	490,000	490,000
Cyanide recovery circuit op. cost/yr	\$430,000	\$460,000
Less costs savings, destr. circuit	\$132,000	\$132,000
Net recovery circuit op. cost/yr.	\$298,000	\$328,000
Recovered NaCN cost	\$0.61/lb.	\$0.67/lb

Although the analysis is a preliminary estimate, several conclusions can be drawn. It appears that cyanide recovery at the Newmont's Midas mine could have some economic advantage, and further evaluation and testwork may be warranted. It could be possible to recover sufficient cyanide from the barren solution to completely eliminate the need for the cyanide destruction circuit. This would increase the recovery circuit costs, but would reduce the destruction circuit costs by about \$0.50/ton of ore treated. There is likely an optimum economic point between the two circuits.

The above comments pertain to the well-established AVR/packed column process. There appears to be a good possibility of solving the one outstanding problem of build-up of pressure in the cyclone assembly and thus reducing the costs of the ASH/CN process. In this case, the economics of the two systems could be very similar.

Since a number of AVR/packed column plants have been built, and the current AVR/packed column cost estimating model has been developed from this plant data, the accuracy of the preliminary cost estimate for the AVR/packed column plants above should be reasonably good. In addition, because several plants have been built and operated, a number of engineering improvements have been built into the system.

The ASH/CN system is still in early stages. Although engineering and design parameters were successfully tested and measured during the pilot test runs at Midas, additional scale-up work, particularly related to the use of larger cyclones/multicyclones, will be required. Further modifications and improvements in circuit design and engineering design will have some effect on both capital and operating costs for a full-scale ASH/CN unit. Most of the equipment for the ASH and AVR/ packed column circuits are identical. At this point it seems reasonable to expect that, for an equivalent pressure drop across each system the capital and operating costs for each will be generally similar.

One of the advantages initially identified for the ASH system was that the system is small and readily transportable, particularly in comparison with the AVR/packed column technology that requires the use of large packed towers and the resultant large concrete foundations and footprint. It was felt that, given equal capital and operating costs, the fact that an ASH/CN unit could be fabricated and assembled completely off-site, then transported and made operational in a very short time period with a small, temporary footprint, would be preferable to several large concrete and steel structures.

A transportable ASH/CN unit could be moved from one site at the end of operations to another site at very little cost. This would not be the case with a traditional AVR/packed column unit. While this is a distinct advantage, salvage value or tear-down cost at the end of a long project would have little effect on the Net Present Value of either in a cash - flow comparison.

Discussions with operating companies have indicated some perception that there is a clear, but perhaps intangible, advantage to operating companies, individually and as a group, in reducing the tonnage of sodium cyanide that is transported on highways from manufacturer to end user. Certainly transport of cyanide has proven very safe over many years of use, but occasional incidents have occurred, and the potential for such incidents is directly proportional to the quantity of cyanide transported. Reuse of cyanide at mine sites would have a major effect on the quantity of cyanide delivered.

Work carried out during this project has dealt with cyanide recovery from clear solutions only. Early project plans included possible work using the ASH system for cyanide recovery from slurries, but the physical configuration and equipment in the available pilot unit (flat-bottomed tanks, pumps not suitable for slurry) made studies in this area impractical.

Although the AVR/packed column system can be applied equally to solutions and slurries, physical (and some chemical) problems have made its use on slurries much more difficult. The AVR/packed column system was originally applied to the treatment of slurries in several locations, but these have since been converted to clear solution applications – primarily for operational reasons.

The ASH might be suitable for use in slurry applications. It was originally developed as a device for the flotation recovery of minerals from ore slurries, and much of the basic structure is very similar to the conventional hydrocyclones widely used as a classification device in mineral processing slurry grinding circuits. Particularly with the current development of the mesh tube, it would appear likely that the ASH/CN system could be readily adapted for use on slurries as well as clear solutions.

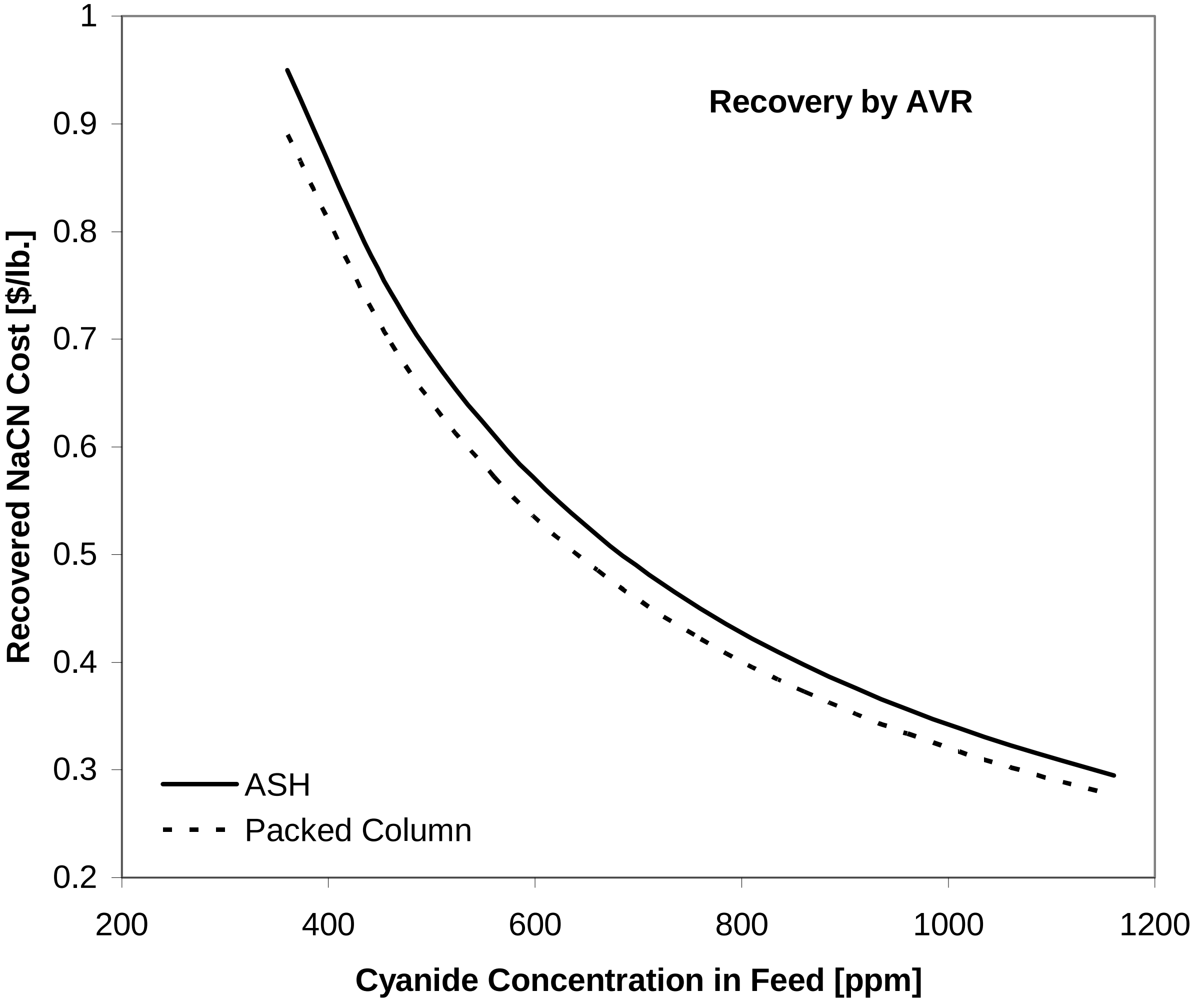


Figure 31. Cost analysis of cyanide recovery as a function of feed concentration assuming a cyanide recovery of 94 %.

10. Conclusions

Significant progress has been achieved towards commercialization of the ASH mobile system for cyanide recovery by the AVR process. Due to reduced gas flow resistance in the air flow system, the air/water ratio for a single ASH unit (Q^*) could be increased to 250, nevertheless, multi - stage stripping system yields better efficiency. The operating parameters of the absorbing ASH indicate that it can replace an absorbing column. Rapid removal (absorption) of over 95% of HCN from the gas phase can be expected in a single stage. Taking into account the fact that HCN re-absorption was carried out in a single ASH, the performance of the unit was exceptionally effective and its potential for industrial application was shown.

For larger Q* the A*ctual Removal* of HCN from the barren solution was better. However, increase of the A*ctual Removal* with increased air flow rate from 60 to 120 was minimal (a few percent). These results indicate that optimum results should likely be obtained by a two- or three-stage stripping system with the Q* in each stage not exceeding 120. This should enable the system to attain the 80-90 % (or higher) overall stripping level necessary in a commercial unit.

Investigation of the permeability of the porous tubes used in the stripping ASH and regenerated by spraying with deionized water allowed to introduce another type of ASH suitable for contacting voluminous stream of gas with small stream of an aqueous phase. A new design of the stripping cyclone included tangential air inlet, larger space between tubes, and several spraying nozzles installed in the cyclone casing. The proposed arrangement is a two to four stage stripping system with one absorption stage. Minimal resistance to flow is obtained by replacement of the porous tube with stainless steel mesh. In order to eliminate the disturbing impact of the incoming gas phase, the gas inlet is made tangential, thus providing much more uniform flow of gas through the mesh.

The new ASH design assures low pressure drop (0.3-0.5psi), allows for larger gas flow rate (easy adjustment of Q*), allows for handy replacement of the porous tube, reduced energy demand, and closed system operation thus avoiding atmospheric pollution.

The 2'' ASH performed much better than the 6'' ASH with respect to residual HCN content and the amount of alkaline solution required. Both the stripping and absorbing ASH units were equipped with stainless steel sparging tubes. Such design alleviated plugging justifying design of fully automated system. Thus the stripping ASH system is becoming competitive with the traditional stripping column. Economical analysis shows that operating and capital cost are similar to AVR/packed column system. However in case of ASH there is still room for improvements which will certainly influence the economics, while conventional pack column system is well known and established thus no significant decrease in costs could be expected.

It is expected that the ASH might be suitable for use in slurry applications. Particularly with the current development of the mesh sparging tube, it would appear likely that the ASH system could possibly be adapted for use on slurries as well as clear solutions.

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