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PROPOSED HCl RECOVERY SYSTEM,
SALT LAKE CITY PILOT PLANT

By
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August 20, 1954

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Pittsburg, California

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TOPICAL REPORT

PROPOSED HCl RECOVERY SYSTEM
SALT LAKE CITY PILOT PLANT

by

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August 20, 1954

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SUMMARY

A design is presented for a system to recover hydrochloric acid currently being wasted in the existing solvent extraction pilot plant in Salt Lake City. The recovery system would serve as a demonstration unit analogous to a similar unit required in any large-scale commercial plant for the purpose of reducing acid costs.

It is estimated that a demonstration unit can be built for \$14,000. It could be included in the present pilot plant site; an additional operator would probably be needed to run the unit.

INTRODUCTION

During the earlier months of 1954 operation was initiated in a pilot plant located at the U. S. Bureau of Mines, Salt Lake City, in order to test Dow's process for recovering uranium and vanadium from carnotite leach liquors by means of solvent extraction. The desired products are obtained as solutions of UO_2Cl_2 or VOCl_2 in 10 N HCl, and one of the final steps in the process involves the evaporation of these solutions to relatively high concentrations.

The initial design of the pilot plant called for batchwise evaporation of the product solutions, with the resultant HCl vapors being dissolved in water and discarded to the sewer. However, the cost of the discarded acid per pound of product is rather high, and any commercially acceptable process must provide for the recovery of the HCl vapors and recycling back to the solvent stripping system.

A system for recovering HCl vapors produced in the existing pilot plant is described herein. It is a small-scale analogue of an HCl recovery system which could be expected to be incorporated in a large commercial plant, with the exception that process variable control is mostly manual rather than automatic.

In the proposed process, the vapors from the evaporators are combined with an HCl make-up vapor which compensates for the HCl lost with the concentrated liquids from the evaporators. The make-up vapor is produced by stripping 22° BeHCl, the most concentrated commercially available HCl solution; during this procedure some constant boiling HCl is also produced and may be discarded or else used to replace an equivalent amount of H_2SO_4 in curing the carnotite ore*. The combined vapors

* All equipment subsequent to the curing step is designed to be resistant to corrosion by HCl.

PROCESS DESCRIPTION

Uranium Evaporation

The various processing steps can be followed by reference to drawing AEC R4-62 on the next page.

10 N HCl, loaded with UO_2Cl_2 , overflows from the first stripping stage settler, T-5A. The acid is metered into the existing stripping system, but periodic adjustment of overflow levels in various stages may cause surges in the final overflow. A surge bottle, T-1S, is therefore required; a constant load upon the uranium evaporator, E-1S, is provided by pumping the pregnant acid stream by means of Brosites pump, P-1S, into an overhead box, X-1S, so that a constant head is maintained above rotameter, RM-1S, which regulates the feed to E-1S.

The pregnant acid stream is greatly concentrated in steam-heated evaporator E-1S. The HCl vapors flow through an overhead glass line into condenser H-4S; the concentrated liquid leaves the evaporator through a constant overflow leg, is cooled in the small cooler, H-1S, and is stored in flask T-2S. The flask is provided with a bottom stopcock to allow periodic withdrawal of liquid into clay dishes for final uranium precipitation.

All vents are connected to a common header which, in turn, is vented as high as possible to the atmosphere. All streams are cooled to minimize the vapor pressure of HCl and eliminate the HCl odor nuisance.

Vanadium Evaporation

The vanadium-pregnant acid stream is evaporated in substantially the same manner as the uranium stream. T-3S, P-2S, X-2S, and RM-2S are used to provide a steady supply to evaporator E-2S, in this case a 5-gallon Pfaudler kettle. The vapor from the evaporator is combined with that from E-1S and condensed in H-4S.

Because of larger cooling requirements, the evaporator product cooler and receiving vessel are combined in the 10-gallon Pfaudler kettle, H-3S. Since, however, the liquid in the constant overflow leg from E-2S is hot, cooling must be provided on the overflow leg vent by means of H-2S; any vapor escaping from the hot liquid should correspond in composition approximately to a constant boiling mixture and should be easily condensed.

are condensed to produce the required amount of 10 N HCl for solvent stripping. The process can be followed by referring to the material balance flowsheet in the appendix.

Two alternate means of adding make-up have been considered:

1. Vapors from evaporators are condensed, and make-up is added as water and anhydrous HCl.
2. Vapors from evaporators are condensed, and 22° BeHCl is added directly as make-up until a 10 N acid is obtained; excess acid is discarded.

Both of these methods were rejected because of higher costs than the proposed process.

The HCl recovery system for the pilot plant has been designed to operate on a continuous basis, since batchwise operation would result in very difficult control problems. Since the pilot plant is operated only one shift per day, the recovery system has been designed to have a small liquid hold-up, so that only a few minutes will be required each day to come to steady state operation.

It should be pointed out that additional data, particularly those concerned with phase equilibria in the concentrated liquor systems, are required to confirm the validity of the design proposed in this report. Phase equilibria studies have been initiated at the Bureau of Mines, and initial results with the uranium liquor indicate that a much richer HCl vapor is obtained during boiling up to relatively large U_3O_8 concentrations than was assumed in calculating material balances in this report. The possibility therefore exists that make-up HCl need not be added as a rich HCl vapor and that the HCl stripping column can be eliminated from the proposed design. The design and cost figures presented herein can thus be considered a maximum.

Figure 1. Proposed HCl Recovery System, Salt Lake City Pilot Plant.

A quick-opening valve in the bottom of H-3S permits periodic withdrawal of liquid for final vanadium precipitation.

HCl Make-up

The required HCl vapor make-up is produced by stripping 22° BeHCl in a system consisting of a reboiler, E-3S (non-agitated 5-gallon Pfaudler kettle) and a 10-plate Oldershaw column, B-1S. The concentrated acid is fed from storage drum, T-4S, through an overhead box system consisting of P-3S, X-3S, and RM-3S, similar to the feed control systems on the uranium and vanadium evaporators. The liquid is introduced into the top of the stripping column, and the desired vapor make-up leaving the top of the column is combined with vapors from the evaporators and condensed in H-4S.

The constant boiling HCl underflow from the reboiler leaves through a constant overflow leg, is cooled in small cooler, H-5S, and collected in rubber-lined drum, T-5S.

HCl Condensation

The combined vapors are condensed in an 18-foot vertical double-pipe Karbate condenser, H-4S; the cooling capacity of the condenser is sufficient to subcool the resulting liquid to room temperature. A vertical film-type condenser is used because of higher heat transfer coefficients obtainable; Karbate is preferable to glass because of much higher thermal conductivity.

The liquid is collected in glass jar, S-1S, which is vented to the atmosphere, and, following continuous flow and specific gravity determinations, is collected in rubber-lined drums, T-6S, AB. From here the 10 N acid can be pumped into existing HCl feed tanks or directly into the solvent stripping systems.

PROCESS CONTROL

Uranium Evaporator

Three requirements are imposed upon the uranium evaporator:

1. Regardless of variations in feed rate, the evaporator must be capable of concentrating the feed to approximately 1500 g of U_3O_8 per liter.
2. Continuous flow of both feed and product is quite small - for design flows, see material balance flowsheet in the appendix. The volume of the evaporator must therefore be small in order to keep the product holdup small, for otherwise too much time would be required to fill the evaporator, and experimental material balances would be more difficult to make.
3. Since the existing pilot plant operates only one shift per day, the evaporator must be started up each morning. It must therefore be small enough so that only a few minutes are required to reach steady state boiling.

The first requirement can be met simply by controlling the boiling temperature in the evaporator, which for the desired concentration is 130°C . Reference to product boiling curves (see appendix) reveals that in the neighborhood of the desired concentration, the boiling temperature changes considerably with slight changes in concentration. Furthermore, in spite of extremely high U_3O_8 concentrations, there is no tendency for uranium salts to crystallize out, either in the hot or cooled product, even at concentrations up to 1500 grams of U_3O_8 per liter.

Any concentration above, say, 1200 grams per liter is satisfactory, since at this point the bulk of the HCl has been evaporated anyway. It therefore follows that the temperature control is not very critical, and it can be accomplished simply in the following manner.

From the generalized heat transfer equation, $Q = UA\Delta T$, it follows that for a constant feed and product, $UA\Delta T = \text{constant}$. Now, suppose the specified design results in a large value of UA , so that the required ΔT is small. This means that the steam pressure in the heat coils and therefore the condensing temperature is held at only a slightly higher level than the boiling temperature. If the reducing valve controlling the

steam pressure is now kept at the same setting, even a considerable change in Q due to a change in feed rate or a change in U due to fouling, results in only a small change in product concentration; i. e., for a given design,

$$\Delta T \sim \frac{Q}{U}$$

and even if $\frac{Q}{U}$ and therefore ΔT suddenly changes, say, twofold, as long operation continues on the steep portion of the uranium boiling curve, the change in uranium concentration is very small.

For example, the heat load Q upon the evaporator corresponding to the design flows is 10,390 BTU/hr. For the specified design, UA is estimated to be 1860. The required ΔT is therefore $10,390/1860 = 5.6^\circ\text{F}$, or 3.1°C . Since the boiling temperature is 130°C , a steam pressure corresponding to a condensation temperature of 133°C must be maintained in the coils.

Suppose, however, that due to fouling or due to an overestimation of U , the product UA is actually only 1000. As a first approximation, Q remains constant, and required ΔT is $10,390/1000 = 10.4^\circ\text{F}$, or 5.8°C . If the steam temperature is still 133°C , the boiling temperature is only about 127°C , and the U_3O_8 concentration is 1485, rather than 1500 g per liter, a negligible change.

Thus, once the proper initial steam setting on the evaporator is determined, feed changes are automatically compensated for.

Since ΔT is small, UA must be rather large. However, the second and third requirements imposed upon the evaporator limit its size, and it follows that A should be small; U must therefore be very large. The only material resistant to HCl having high overall heat transfer coefficients is tantalum. A satisfactory evaporator can be constructed from a section of 6-inch glass pipe into which a 9-foot long coil of $5/8$ inch o. d. tantalum seamless tubing has been inserted.

If 10 inches of liquid are maintained in such an evaporator, the total holdup is about 1.10 gallons, or a little over one day's production at design flows. If the steam reducing valve is kept at its steady state setting, about 8 minutes are required to bring the evaporator contents from room temperature to a steady state boil.

Vanadium Evaporator

Requirements similar to those imposed upon the uranium evaporator are also imposed upon the vanadium evaporator. However, because of the much smaller solubility of VOCl_2 , the pregnant liquor cannot be concentrated to more than about 250 grams of V_2O_5 per liter, for otherwise VOCl_2 would crystallize out in the equipment, especially following cooling. Thus a definite limit is imposed upon the degree of concentration, even though some crystallization could be tolerated following cooling. On the other hand, the more the liquor is concentrated, the more HCl vapor is driven out of it and recovered. An optimum operating point therefore exists, and it follows that a much closer temperature control is required than was the case with uranium evaporation.

Because of larger flows, small commercially available equipment can be used for evaporation. A 5-gallon agitated Pfaudler kettle has sufficient heat transfer area to transmit the design heat load (18,400 BTU/hr), provided a sufficiently high ΔT is maintained. The boiling temperature, approximately 115°C , must be held relatively constant by means of a temperature sensitive element activating a regulator valve on the steam jacket inlet. The temperature is regulated by presetting the pressure upon a diaphragm opposing the vapor pressure of the liquid in the temperature sensitive element; the correct setting must be determined by trial and error every time the flow into the evaporator is changed.

HCl Make-up

The purpose of the HCl make-up system is to obtain an acid out of H-4S which is of the proper gravity and flows at just the right rate to allow feeding back into the solvent stripping systems without further adjustment. The required acid conditions must be satisfied no matter what the rate and composition of the vapors from the evaporators are; as a matter of fact, these will usually be unknown. A scheme must therefore be devised which will allow automatic regulation of the vapor overhead from the HCl stripping system so that the acid resulting from the condensation of all combined vapors meets the required feed conditions to the stripping system. An indication as to whether these conditions are satisfied is given by a rotameter and a continuous specific gravity meter on the discharge from the condenser; on the basis of readings obtained, the operator* must decide how to adjust the HCl stripping system.

* In a large-scale plant, the operator would be replaced by automatic control instruments.

Under design conditions of flow (see material balance flowsheet), three theoretical plates are required to produce the desired vapor overhead and constant boiling HCl underflow from 22°BeHCl feed. If now column B-1S is oversized and more theoretical plates are used, even if it should be required that the overhead vapor be very rich in HCl, the column will have sufficient fractionation capacity to give a constant boiling HCl underflow; as a rule, the bottom plates will operate close to the azeotropic "pinch point" and will be doing little work. Provision of ten actual plates should result in at least five theoretical plates.

Thus, the liquid in the reboiler, E-3S, will always be constant boiling HCl, no matter what the requirements as to overhead composition and rate may be. A process variable is thus automatically eliminated, and the conditions of the overhead can be controlled at will by varying the feed rate of 22°Be acid and the reboil heat.

Over the range of overhead compositions expected, and with the composition of the underflow constant, it turns out that the overhead rate is substantially proportional to the reboil heat. The overhead rate can therefore be controlled by means of the pressure reducing valve on the reboiler steam jacket inlet. Now, the operator does not know what pressure to regulate at in order to get the desired reboil heat and therefore overhead rate.* However, it is not necessary to know this, for it is required simply to change the setting on the reducing valve until rotameter RM-4S indicates the desired flow.

With the underflow composition constant and the overhead rate controllable, it follows from a material balance around the stripping column that the overhead composition can be varied directly by varying the feed into the column.

* It should prove helpful to determine, when the system is first started up, what the expected steam pressure range will be. The relationship between steam temperature corresponding to the regulated pressure and the reboil heat is $Q_{REB} = U_R A_R (T_{\text{steam}} - 226)$, where $A_R = 3.5 \text{ ft}^2$ for a 5-gallon Pfaudler kettle, and 226 is the constant underflow temperature.

During operation of the HCl make-up system, therefore, it is necessary to observe the readings of the rotameter and gravity meter on the condenser discharge. The rotameter reading is brought to the required mark by turning the steam reducing valve, and the gravity meter reading is brought to the desired point by turning the throttling valve on RM-3S.

COST ESTIMATE

Cost of equipment in the existing pilot plant available for use in the HCl recovery system is not included.

Cost of equipment, uninstalled*	\$6,100
Cost of instruments, uninstalled*	1,200
Cost of piping, uninstalled	900
	<hr/>
Cost of equipment to be purchased	\$8,200
+ 25% contingency	
Say	<u>\$10,000</u>

To this add -

Cost of construction materials	\$ 500
Cost of engineering & procurement	1,000
Construction labor estimated at	
480 man-hours at \$5/hr	2,400

TOTAL COST OF PLANT, SAY, \$14,000

Acid cost saving achieved by recovery unit: Assume acid costs for both uranium and vanadium are lumped onto the uranium.

Daily U_3O_8 production (8 hrs) = 6.45 lbs.

With no HCl recovery, 48 gallons per day of 20° BeHCl are required. Cost in car lot quantities (to correspond with large plant requirements) is 1.5¢/lb., or 14 1/2¢/gallon.

∴ Acid cost/lb U_3O_8 = $14 \frac{1}{2} \times 48/6.45 = \$1.08/\text{lb.}$

With HCl recovery, 100 lb/day of 22° BeHCl are required. Cost is 1.75¢/lb.

∴ Acid cost/lb U_3O_8 = $1.75 \times 100/6.45 = 27\text{¢}/\text{lb.}$

Saving = 81¢/lb. of U_3O_8

* See Appendix for breakdown

APPENDIX

Equipment Description

<u>Designation</u>	<u>Description</u>	<u>Cost</u> <u>(uninstalled)</u>
<u>Columns</u>		
B-1S	10-plate Oldershaw column, 3-in. diameter, without vacuum jacket, but with magnesia insulation.	200.00
<u>Evaporators</u>		
E-1S	Uranium evaporator, made from 16-in. section of 6-in. glass pipe, with 9 ft. of 5/8-in. i.d. tantalum seamless tubing, 0.015" thick, bent into 5-in. steam coil. 1/4-in. tantalum thermowell for iron-constantan thermocouple. 1-in. magnesia lagging.	430.00
E-2S	Vanadium evaporator, 5-gallon Pfaudler jacketed glass-lined kettle, with 2-blade agitator, and baffle with thermowell.	1,500.00
E-3S	Reboiler, 5-gallon Pfaudler jacketed glass-lined kettle.	1,020.00
<u>Heat Exchange Equipment</u>		
H-1S	Uranium product cooler; 600-mm Graham condenser	9.73
H-2S	Cooler in vanadium overflow vent line; 600-mm Liebig condenser.	7.98
H-3S	Vanadium product cooler and receiver; 10-gallon Pfaudler jacketed glass-lined kettle, with 2-blade agitator, baffle with thermowell, and quick-opening bottom valve.	1,600.00
H-4S	HCl vapor condenser; double-pipe Karbate exchanger, 18 ft. high, 1" i.d. inner pipe, 2" i.d. outer pipe.	150.00
H-5S	Constant boiling HCl cooler; 600-mm Graham condenser.	9.73

<u>Designation</u>	<u>Description</u>	<u>Cost</u> <u>(uninstalled)</u>
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Pumps

P-1S	Uranium liquor feed pump and spare; Model R "2 in 1" Brosites proportioning pump.	393.60
P-2S	Vanadium liquor feed pump; Brosites proportioning pump.	196.80
P-3S	22°Be HCl feed pump; Brosites proportioning pump.	196.80
P-4S	10 N HCl transfer pump, model No. P30 Vanton "Flex-i-liner" pump.	256.00

Separators

S-1S	10 N HCl collection and vent jar, glass	50.00
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Tanks

T-1S	Uranium liquor surge pot; 5-gallon solution bottle	8.00
T-2S	Uranium product receiver; 4-liter Erlenmeyer flask with bottom stopcock.	12.50
T-3S	Vanadium liquor surge pot; 5-gallon solution bottle.	8.00
T-4S	22°Be HCl storage; 55-gallon rubber-lined drum.	Existing
T-5S	20% HCl storage; 55-gallon rubber-lined drum	Existing
T-6S, AB	10 N HCl storage; 55-gallon rubber-lined drums	Existing

Miscellaneous Equipment

X-1S	Overhead boxes, plexiglass, 4" x 4" x 4"	30.00
X-2S		
X-3S		

TOTAL UNINSTALLED EQUIPMENT COST:

\$6,079.14

Instrument Description

Temperature recorders on E-1S, E-2S, and H-3S; Brown indicating electric control millivoltmeter pyrometers, with iron-constantan thermocouples. Two existing.	\$ 189.00
Reducing valves on E-1S and E-3S; 1/4-in. Leslie pressure reducing valves, type J-1.	90.00
Steam pressure gauges on E-1S, E-2S, and E-3S.	93.00
Four all-glass rotameters (RM-1 to 4) with Hastelloy C floats.	200.00
Temperature regulator on E-2S, type JTCO 1/4-in. Leslie regulator.	140.00
S and K all-pyrex continuous specific gravity meter.	450.00
TOTAL UNINSTALLED INSTRUMENT COST:	\$1,162

Utilities

Steam (80 psig)

E-1S	11.2 lbs/hr
E-2S	20.2 lbs/hr
E-3S	9.9 lbs/hr

TOTAL:	41.3 lbs/hr
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Cooling water

H-1S	2 GPM
H-2S	2 GPM
H-3S	3 GPM
H-4S	7 GPM

TOTAL:	14 GPM
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Figure 2. Material Balance Flowsheet, HCl Recovery System.

Figure 3. Product Boiling Curves.

August 1, 1954

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