

Selenium Analysis

D.G. Biechler, D.A. Ward and G.E. Van De Steeg

Regulatory Agencies (NMEID and USEPA) are considering establishing regulations requiring that concentration of selenium in water released to groundwaters and/or aquatic environments is 50 ug/l or less. Meeting such a regulation requires an accurate, precise, and highly reproduceable system of analyses. Such a system ought to be acceptable to the agencies involved and capable of duplication by laboratories equally skilled in analyses. Recognizing that the minerals present in the Ambrosia Lake area contained significant quantities of selenium, it was deduced that mine water discharges from this area would be greatly influenced by these proposed regulations. Consequently, an investigational program was initiated to establish analytical procedures meeting the requirements.

Investigative Results.

Over a period of approximately two years, the Kerr-McGee Technical Center (KMTC) has evolved a system, improved the method, demonstrated its reliability, and examined many of the parameters which affect the accuracy and precision of the measurement system.

Selection of Method.

The preferred method of selenium analysis is neutron activation requiring a large, highly stable source of thermal neutrons, available at few laboratories, which converts the selenium to selenium-75 with a half life of 120 days. Subsequent to this conversion and a decay period, samples can be directly counted on a Ge(Li) detector coupled with a multi-channel gamma ray spectrometer. Such analytical instruments are extremely expensive and available to only a few highly

specialized laboratories such as exist at federally financed, reactor research centers. The authors know of no commercial laboratory offering this service for environmental levels of selenium in the range of 10 ug/l or less. Since the preferred method was not available to the KMTC, remaining analytical systems available were atomic absorption (graphite furnace or hydride generation), fluorometric or colorimetric methods.

Fluorometric or colorimetric methods have traditionally suffered interferences when used for environmental analysis with levels of contamination with other metallic ions. Consequently, the KMTC was forced to rely upon the methodology of atomic absorption spectroscopy, preferably using the high temperature graphite furnace method. The KMTC was equipped for hydride generation with subsequent atomic absorption spectroscopy but believes for a routine method this system offered a unnecessary operation hazard to the analyses. The KMTC believed that the graphite furnace method could be demonstrated to be reliable.

The colorimetric procedures given in the "Standard Method for the Examination of Water and Wastewater", 13th edition, 1971, is extremely time consuming, subject to interference, and relatively insensitive, thus requiring large volumes of samples. OSHA has listed the colorimetric agent, diaminobenzidine, as a possible carcinogen further reducing its desirability.

Analyzing samples for selenium content at environmental levels with the graphite furnace atomic absorption method required certain modifications in technique and equipment available to the KMTC. Selenium peaks usually occur in less than one second and the strip chart recorder supply is too slow to record the entire peak resulting in values with a low bias. Strip chart recorders must be replaced with an oscilloscope incorporated into the electronic circuit as a readout, or a micro-

processor with the capability to integrate total peak, thus providing sufficiently sensitive recording.

Since the KMTC instrument was in general use for many metallic compounds, it was determined that the nickel nitrate matrix modifications as described by Martin, Koop, and Ediger (1) could not be employed. Nickel nitrate added to the matrix for water, wastewaters, sediments and sludges, allows higher charring temperature thus volatilizing the majority of the sample. Use of the .1% nickel solution, however, contaminates the graphite furnace for subsequent samples or same samples. An alternative is magnesium, since it is a water cation and seldom requires graphite furnace analyses in the analysis requested of KMTC. It was investigated and has proven to be a satisfactory choice for samples matrix modifications. Magnesium nitrate modifier provides increased sensitivity and charring temperature as demonstrated by Table I and Graphs 1 and 2.

Clear interferences exist which bias the use of either a nickel or magnesium nitrate matrix modifier. Dissolved solids or sulfate concentrations above 1000 mg/l should be subjected to a modified procedure. The KMTC has found the method of standard addition, as shown on Graph 3, to be reliable in establishing the degree of bias in the presence of sulfate.

Failure to use either magnesium or other nitrate as a matrix modifier always produces a low bias in the analysis of environmental samples due to loss of selenium from the graphite furnace during the charring cycle. An acceptable charring program must be used with samples containing appreciable TDS or smoke will be liberated during the atomization cycle at 2400°C, resulting in light

TABLE I

Magnesium Nitrate vs. Nickel Nitrate Sensitivity

	Magnesium Nitrate Addition Absorbance	Nickel Nitrate Addition Absorbance
100 micrograms/liter Selenium Standard	.127	.089
Section 35 Water	.042	.029
Section 36 Water	.041	.026
Section 35/36 Water	.072	.049
Church Rock I Water	.040	.023
Rio Puerco Water	.010	.007
Jacobs Ranch Water	.009	.006

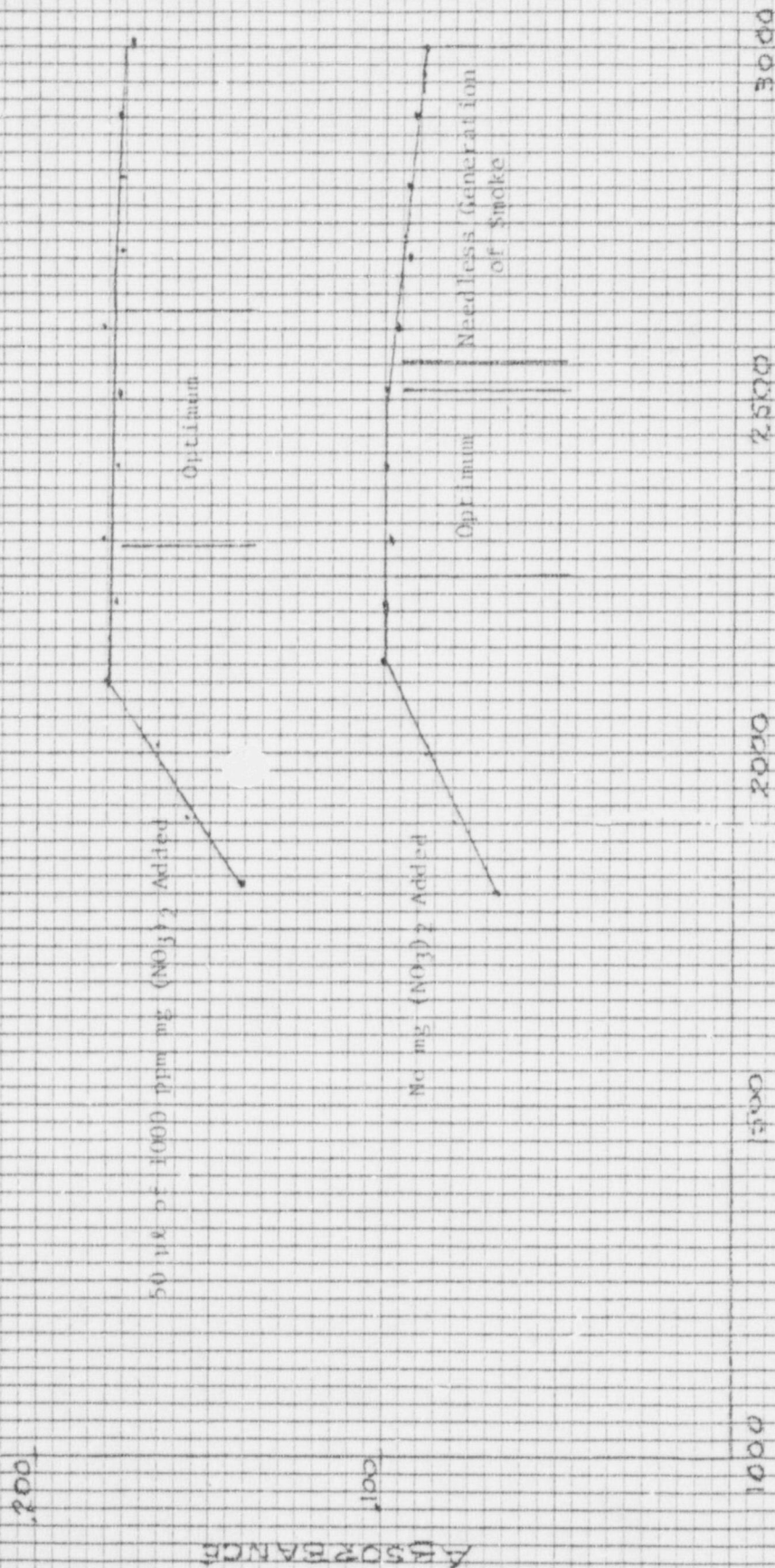
Graph 1

Atomization Temperature vs Absorbance

P.E. 460 MAS

HGA - 76B Graphite Furnace

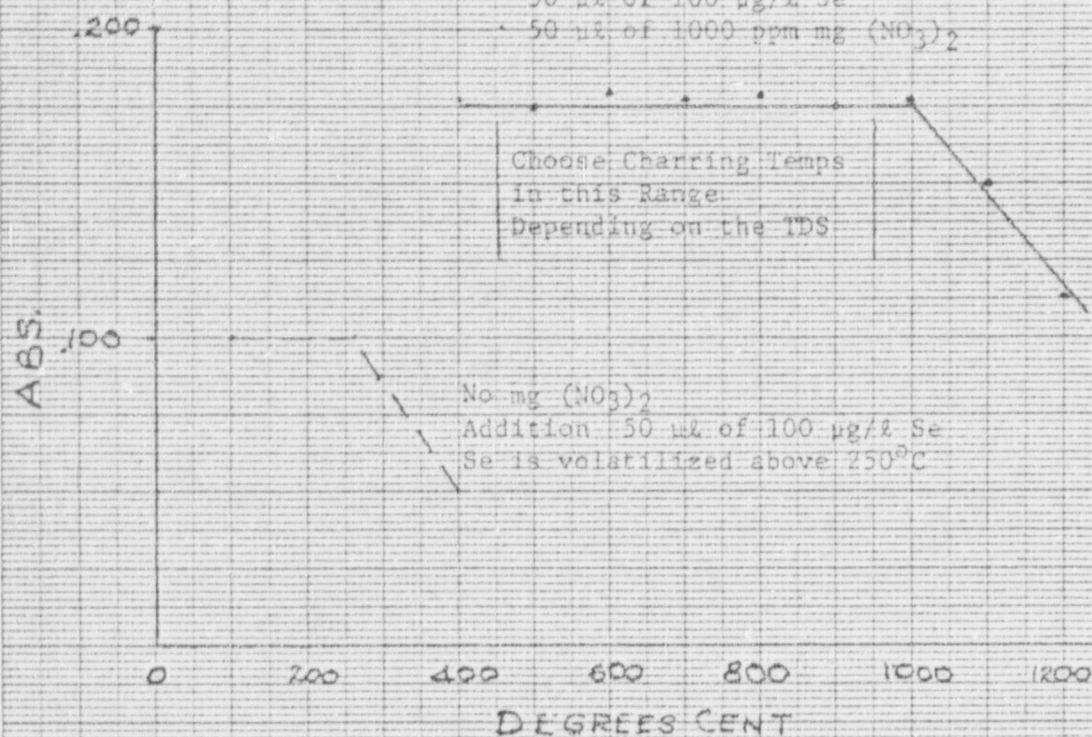
50 μ l of 100 μ g/l Se



Graph 2

Charring Temperature vs Absorbance

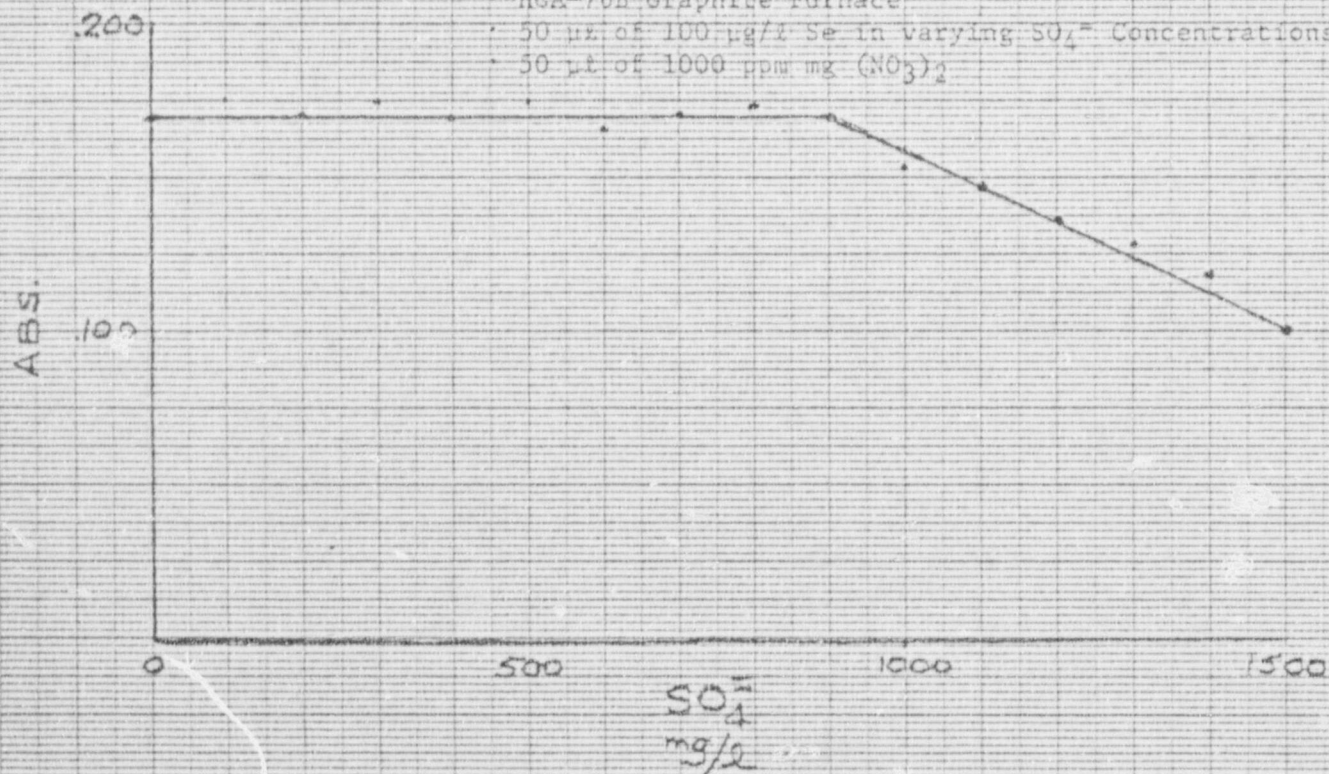
- 2400°C Atomization Temp.
- P.E. 460 AAS
- HGA-76B Graphite Furnace
- 50 μ l of 100 μ g/l Se
- 50 μ l of 1000 ppm mg $(\text{NO}_3)_2$



Graph 3

mg/l SO_4^{2-} vs Absorbance

- 2400°C Atomization Temp./1000°C Charring Temp.
- P.E. 460 AAS
- HGA-76B Graphite Furnace
- 50 μ l of 100 μ g/l Se in varying SO_4^{2-} Concentrations
- 50 μ l of 1000 ppm mg $(\text{NO}_3)_2$



scattering and high results. Improper temperature programing can result in light scattering and high results even with the use of deuterium arc background correction.

The use of an electrodeless discharge lamp as a high intensity source is necessary for an adequate signal/noise ratio. Hollow cathode lamps, which are still commercially available, do not produce an adequate output for trace selenium determinations.

Sample Filtration Procedures.

Very early in the program development, anomalous answers from two laboratories using approximately the same procedures demonstrated an erratic bias between duplicates. This bias appeared to be caused by the difference in the procedures observed prior to analyses. The investigations determined the primary cause, in addition to different quality of operations and the experience of the operator, to be the sample treatment; in one case the samples were filtered and in the other they were not. However, filtration alone did not satisfactorily explain this difference. It is suspected that on raw samples, both selenium+4 and selenium+6, exist with the selenium+4 being present as a finely-divided solid, perhaps a colloid, which apparently can be removed by micro-filtration. Consequently, samples are routinely filtered through a 0.45 micron Millipore or Nucleopore filter, acidified with 0.5 volume percent nitric acid and refrigerated. These samples are then used for soluble selenium determinations.

Total Selenium Analysis.

Raw samples are acidified to 0.5 volume percent nitric acid without filtering and allowed to stand overnight. An oxidation step is needed prior to the analysis. The step requires digestion in a mixture of hydrochloric and nitric

acids except when excess organic material is present which would result in charring. During digestion, a strong oxidizing condition must be maintained. Permitting the digesting solution to reach reducing conditions may result in the loss of selenium and subsequent biasing of the total selenium determination. Total selenium is determined upon completion of the analyses. Suspended selenium is determined by subtraction from the raw value, the value for the filtered sample taken in the field.

Storage and Preservation.

The nitric acid treatment described above, slows the loss of selenium by adsorption into the walls of some container materials. Samples require special treatment to remove adsorbed selenium from container surfaces. Samples one week old or less suffer negligible loss. A storage container should be rinsed with 5 ml portions of nitric acid and allowed to stand for 5 minutes and the volume resulting from three rinsings diluted to normal volume and analyzed by atomic absorption.

The preferred container is linear polyethylene (LPE) as demonstrated by the National Bureau of Standards. Their tests show that conventional polyethylene (PE) yielded 3×10^{-9} g/cm² selenium when leached for 1 week with 50% nitric acid. Under the same conditions, LPE gave only 0.4×10^{-9} g/cm² selenium (1). Conventional polyethylene bottles would result in a 12% increase in selenium content at 20 ug/l concentration while LPE would bias the value only 1.5% at the same level.

Verification of the Selected Method.

Upon selection of the method of graphite furnace atomic absorption, the KMTC then proceeded to establish its reliability internally and externally. Table

III presents the determination of analytical precision on 7 samples of both standards and environmental samples.

During the two year period, that this procedure has been in effect, standard quality assurance procedures were used employing EPA reference samples. The result of this program is given on Table IV.

The Oklahoma Water Resources Board conducts a certification procedure for water analyses laboratories in the State. The State procedure uses the sample mean from all of the laboratories as the control value calculating standard deviation around this mean. The KMTC value has routinely been within one standard deviation of the sample mean as shown on Table V. However, in the evaluation of the December, 1977 data, as compared with our QA procedures using EPA sample data as a control, KMTC believes that the true value is 367 mg/l plus or minus 21 mg/l selenium rather than the value shown.

In addition to the QA procedures, a cooperative study program was established with 6 other laboratories in order to evaluate the comparison of other methods and techniques. Samples for this series were prepared by using the discharge water from Section 35/36 treatment plant and mixing a master solution. Samples to be distributed were composed from 16 liters of Section 35/36 discharge water, thoroughly mixed and separated into 3 five-gallon mixing carboys. Two of the carboys were spiked as shown on Table VI with a standard selenium solution. After mixing, aliquots were removed into linear polyethylene (LPE) containers which had been filled with dilute nitric acid solution for 24 hours and rinsed three times with high purity water. An aliquot was analyzed by graphite furnace atomic absorption and hydride generation atomic absorption. The analysis shown on Table VII gives the results from these two methods. Upon completion of

TABLE III

Analytical Precision of the Recommended Graphite Furnace Atomic Absorption Procedure

Sample Number	Micrograms Per Liter Selenium (5 Observations)	Sample Mean	Coefficient of Variance	Standard Deviation
Section 19-6000	33; 35; 33; 32; 34	33.4	3.4	1.1
Section 35-3300	328; 336; 326; 330; 339	331.8	1.7	5.5
Section 35-6000	93; 95; 97; 94; 94	94.6	1.6	1.5
Section 35-7400	79; 81; 78; 82; 84	80.8	3.0	2.4
Environmental Protection Agency #1 Ref. Sample #575 - 5.2 Micrograms Per Liter Selenium	6; 7; 6; 6; 7	6.4	8.6	0.6
Environmental Protection Agency #2 Ref. Sample #575 - 26 Micrograms Per Liter Selenium	25; 22; 26; 24; 23	24.0	5.4	1.6
Environmental Protection Agency #3 Ref. Sample #575 - 44 Micrograms Per Liter Selenium	45; 47; 44; 46; 45	45.4	2.5	1.1

Note, the precision of the technique is best at high concentration ranges.

TABLE IV

E.P.A.* Water Reference Sample Data Concerning Selenium - KMTC Quality Control

E.P.A. Reference Sample No.	Notebook Reference	Analyzed	Value	Accepted Value
Sample #1171 - #1	612-DAW-12 p95	2/11/77	5.	5.
Sample #1171 - #2	612-DAW-12 p95	2/11/77	17.	16.
Sample #1171 - #3	612-DAW-12 p95	2/11/77	50.	48.
Sample #1171 - #1	612-DAW-12 p122	5/02/77	5.	5.
Sample #1171 - #2	612-DAW-12 p122	5/02/77	19.	16.
Sample #1171 - #3	612-DAW-12 p122	5/02/77	44.	48.
Sample #1171 - #1	612-DAW-12 p131	6/28/77	6.	5.
Sample #1171 - #2	612-DAW-12 p131	6/28/77	15.	16.
Sample #1171 - #3	612-DAW-12 p131	6/28/77	51.	48.
Sample #1171 - #1	612-DAW-12 p155	11/22/77	5.	5.
Sample #1171 - #2	612-DAW-12 p155	11/22/77	15.	16.
Sample #1171 - #3	612-DAW-12 p155	11/22/77	54.	48.
Sample #575 - #1	760-DAW-15 p13	5/16/78	5.	5.2
Sample #575 - #2	760-DAW-15 p13	5/16/78	25.	26.
Sample #575 - #3	760-DAW-15 p13	5/16/78	46.	44.

*Environmental Protection Agency

TABLE V

Date of Analysis	KMT Value (micrograms per liter selenium)	O.W.R.B. Statistically Accepted Value (Microgram Per Liter Selenium)	
		Sample Mean	± 1 Standard Deviation
June, 1975	40	42.9	± 3.9
December, 1975	31	43.	$\pm 16.$
June, 1976	42	51.3	± 16.4
December, 1976	170	207.	$\pm 37.$
June, 1977	230	243.	$\pm 45.$
December, 1977	367	324.	$\pm 61.$
June, 1977	450	483.	$\pm 112.$

TABLE VI

Collaborative Selenium Program Sample Preparation

Sample Number	Milliliter of 1000 Milligrams Per Liter Selenium Added to 16 Liters of Section 35/36 Discharge Water	Final Selenium Concentration
A-1	5.00 milliliters	neat + 312.5 micrograms per liter selenium
A-2	none	neat
A-3	1.00 milliliter	neat + 62.5 micrograms per liter selenium

TABLE VII

Analysis of KMTC Selenium Collaboration Study Water Samples A-1, A-2 and A-3

Sample Number and Description	Theoretical Micrograms Per Liter Selenium Calculated Using the Neat Value of 21 Micrograms Per Liter Selenium and Known Addition Values	Graphite Furnace AAS vs. Standards	Hydride Generation AAS vs. Standards
A-1 (neat + 312.5 micrograms per liter selenium)	333.5	335; 339; 330	340.
A-2 (neat)	21.	21; 20; 21	22.
A-3 (neat + 62.5 micrograms per liter selenium)	83.5	84; 87; 85	82.

this preparation, aliquots were distributed to the seven laboratories shown and the results reported are tabulated on Table VIII.

Examination of the data given on Table VIII demonstrates the difficulty of evolving a reliable analytical system. It has been the experience at the KMTC that accurate, precise analysis can only be achieved with a sampling and handling procedure that is well documented and followed in the field plus a thoroughly experienced analyst on the particular technical procedure in use, supported by a sound quality assurance program. The results shown are not intended to impune any laboratory methods or techniques but to merely demonstrate that even with laboratories with relative continual experience in the analytical system, extreme variation can be expected.

Conclusion.

After two years of continual review, examination of data, modification of methods and stricted adherence to such methods, KMTC has shown that establishment of an accurate, precise and reproducible system of analysis is very difficult. The system adopted by every laboratory concerned must provide for stringent quality assurance for all steps involved. The system developed as a result of this work by KMTC seems reliable and can be duplicated by others.

TABLE VIII

Results of the Kerr-McGee Technical Center Collaborative Selenium Study Program

GF-AAS (Graphite Furnace - Atomic Absorption)
HG-AAS (Hydride Generation - Atomic Absorption)

Laboratory	Analysis	Method	Sample Treatment	Results $\mu\text{g}/\text{kg}$ Se		
				A-1	A-2	A-3
KM Grants KM Grants	2-16-78 2-16-79	GF-AAS(1) GF-AAS	As Received Container-Acid Leached	139. 140.	76. 69.	92. 94.
Univ. of Calif. at San Diego LaJolla, CA	2-06-78 2-06-78	Fluorimetric(2) Fluorimetric	As Received Container-Acid Leached	326.7 326.5 318.9 332.1 326.4	5.5 5.5 5.4 5.9 5.7	69.5 69.2 68.1 72.8 73.8
Bureau of Mines, Socorro, NM	2-13-78	Colorimetric(3)	As Received	203.	69.(4)	21.(4)
United Nuclear Homestake Partners, Grants, NM	2-17-78 2-17-78	GF-AAS GF-AAS	As Received Container-Acid Leached	196. 187. 194.	17. - 19.	53. 47. 48.
Controls for Env. Pollution, Santa Fe, NM	2-13-78	GF-AAS(5)	As Received	300. 350.	9. 10.	56. 68.
KM Technical Center (KMTCC) (6)	2-16-78 2-16-78	GF-AAS GF-AAS	As Received Container-Acid Leached	330. 374.	23. 23.	83. 87.
NM Env. Imp. Agency, Albuquerque, NM	2-17-78 2-17-78	GF-AAS GF-AAS	As Received Container-Acid Leached	310. 324.	12. 10.	100. 102.
The value of the prepared standards				333.5	21.(7)	83.

T. : VIII (Continued)

- (1) Graphite Furnace - Atomic Absorption
- (2) Olson, O. E., JAQAC, Vol. 52, No. 3, 627-634, 1969.
- (3) Using 2, 3 - Diaminonaphthalene. A second set of samples was forwarded due to large sample switch.
- (4) Suspected sample switch.
- (5) Hydride Generation - Atomic Absorption
- (6) Run by an independent operator at Kerr-McGee Technical Center not knowledgeable of sample Se concentrations.
- (7) As-received Grants Section 35-36 mine water discharge.

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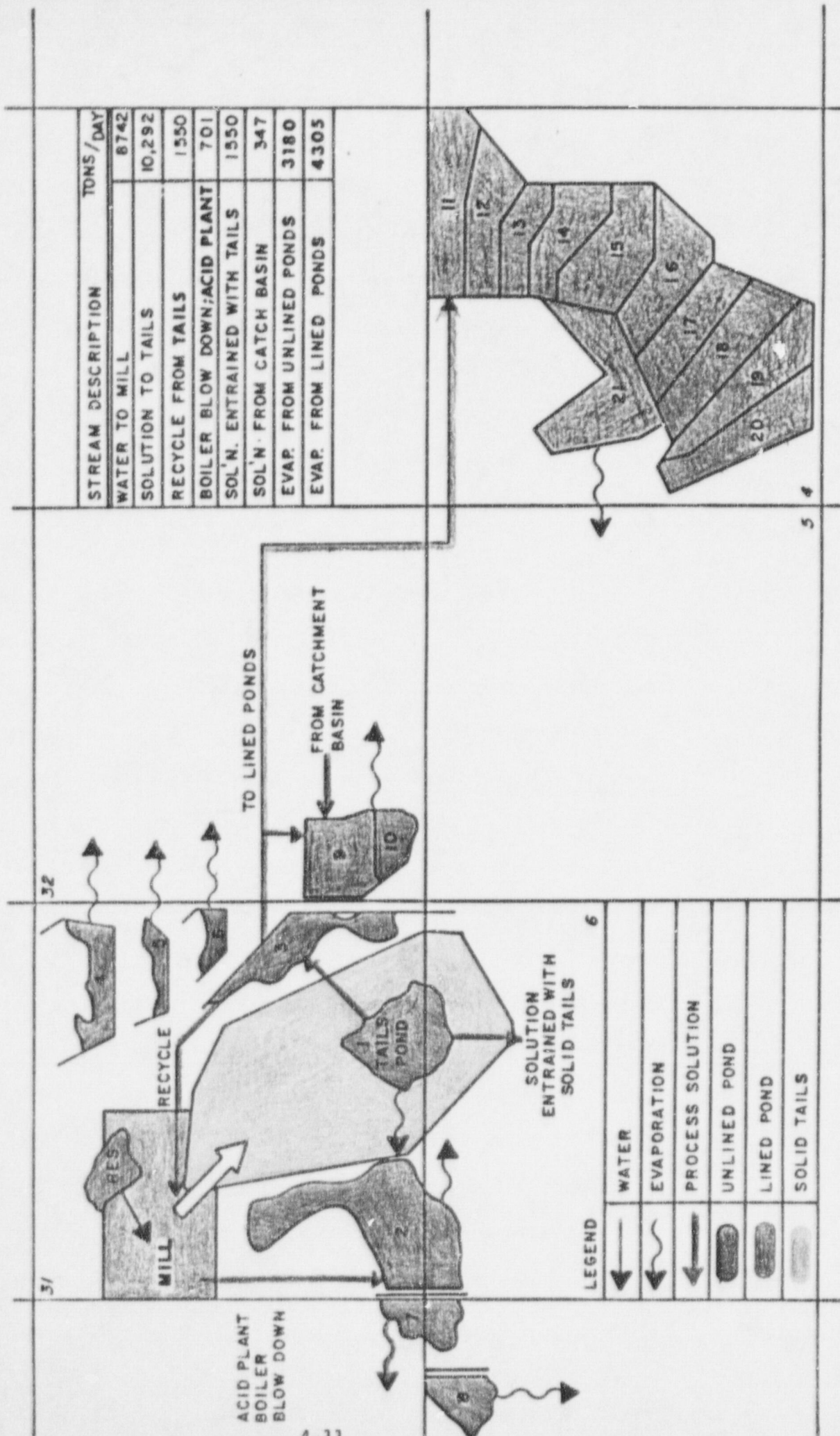


FIG. 4-1

4.5 Backfill

Quivira Mining Company has engaged in the practice of backfilling mine stopes in which the mineral values have been exhausted by physical mining with washed tailings since the early 1960s. Backfilling of exhausted stopes is widely practiced by the mining industry in order to permit the more complete removal of the mineral values from a seam or vein. As used at Ambrosia Lake, backfilling is practiced in order to prevent surface subsidence, intermixing of aquifers, to protect miners and to allow for more complete removal of mineral values from locations in the formation.

Preparation of the sands for backfilling consists of the separation of the coarse fraction from the tailings by using a counter-current decantation circuit. This process provides a relatively clean coarsely-ground material after five stages of counter-current washing with raffinate from the extraction plant. The clean sand is removed to a storage area and subsequently transferred to the designated mine by truck and stored there at ground level. When a backfilling campaign is planned, the sand is loaded into a feed hopper where it is mixed with mine water to the appropriate density, (i.e., approximately 40 percent solid), and permitted to flow down a pipe in shaft or a cased drill hole to the designated stope. A stope is first prepared by bulkheading certain access ways with timber covered with burlap. The backfilling slurry is introduced behind this bulkhead and as the slurry fills the stope the backfilling is interrupted until the material placed is given an opportunity to drain. The dispersing nozzle is then moved to a

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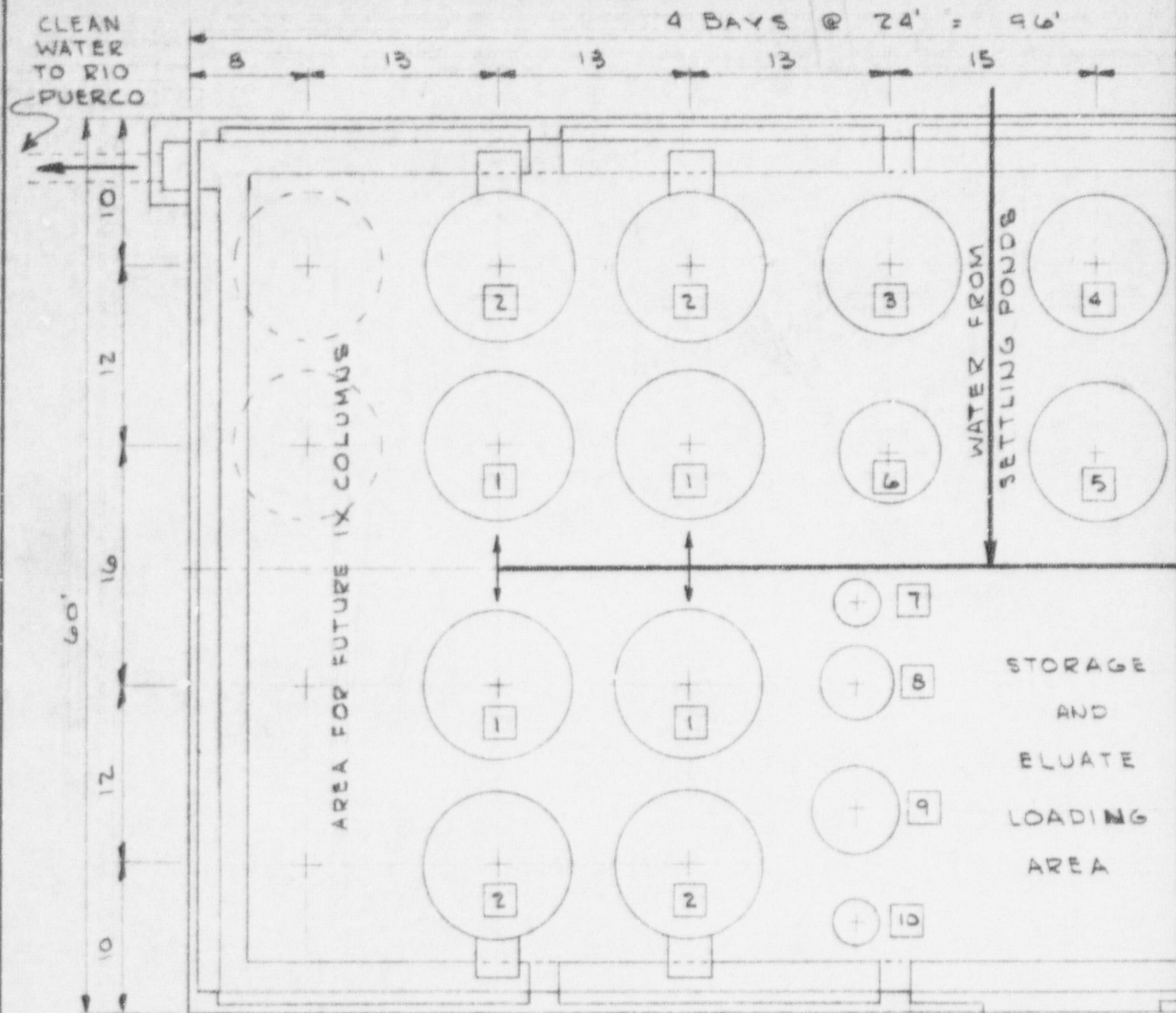
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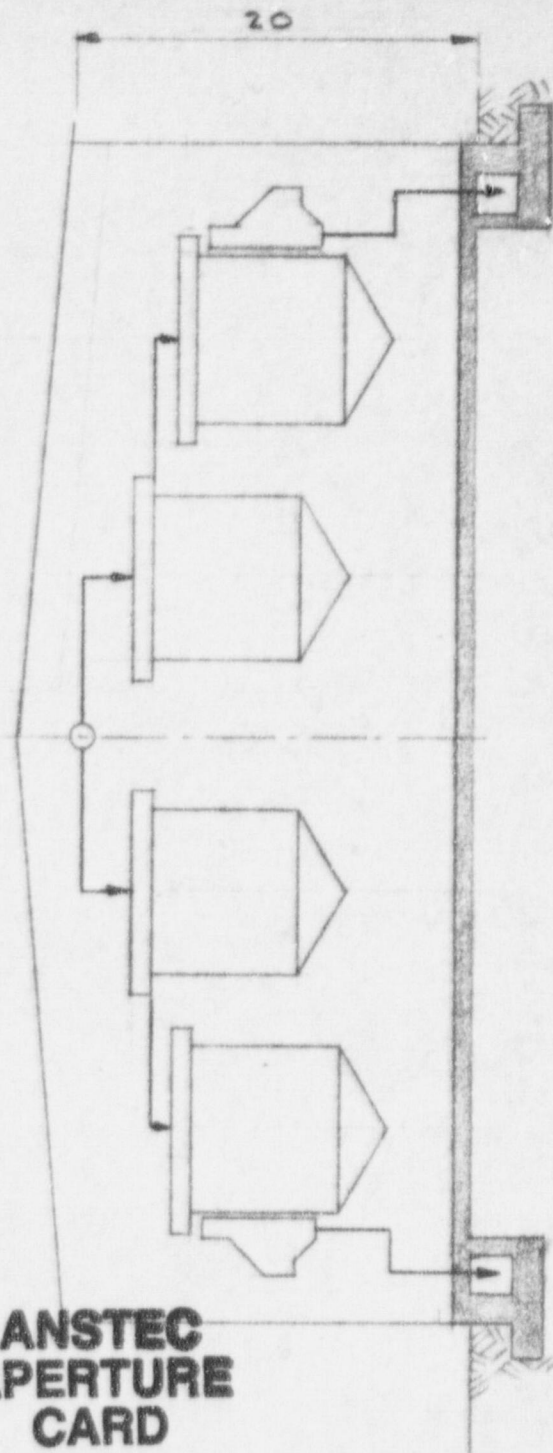
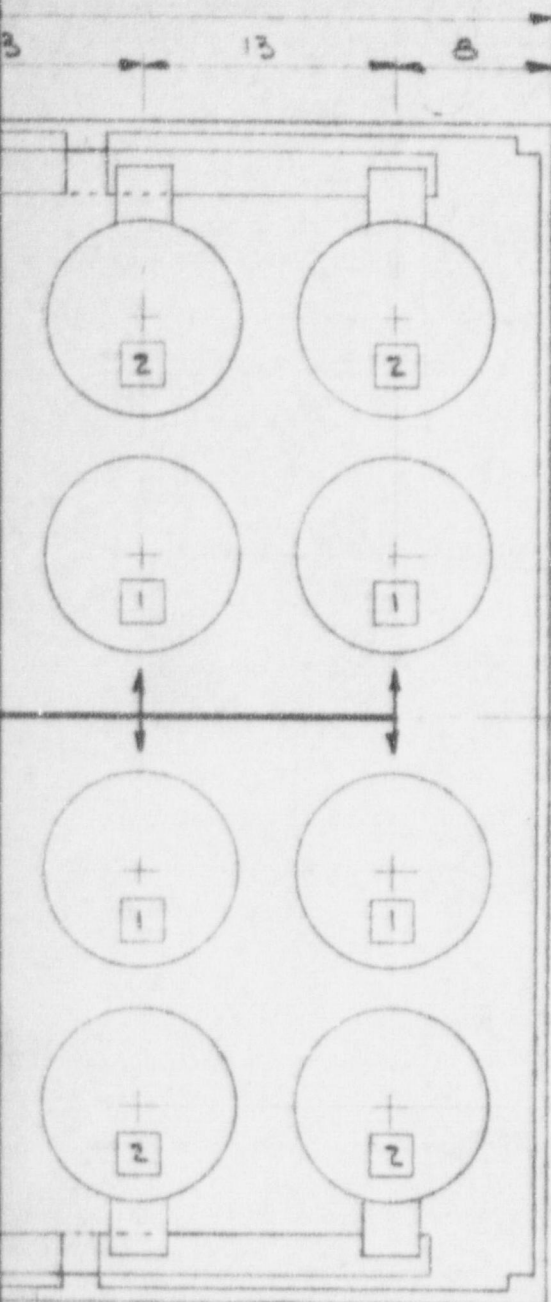
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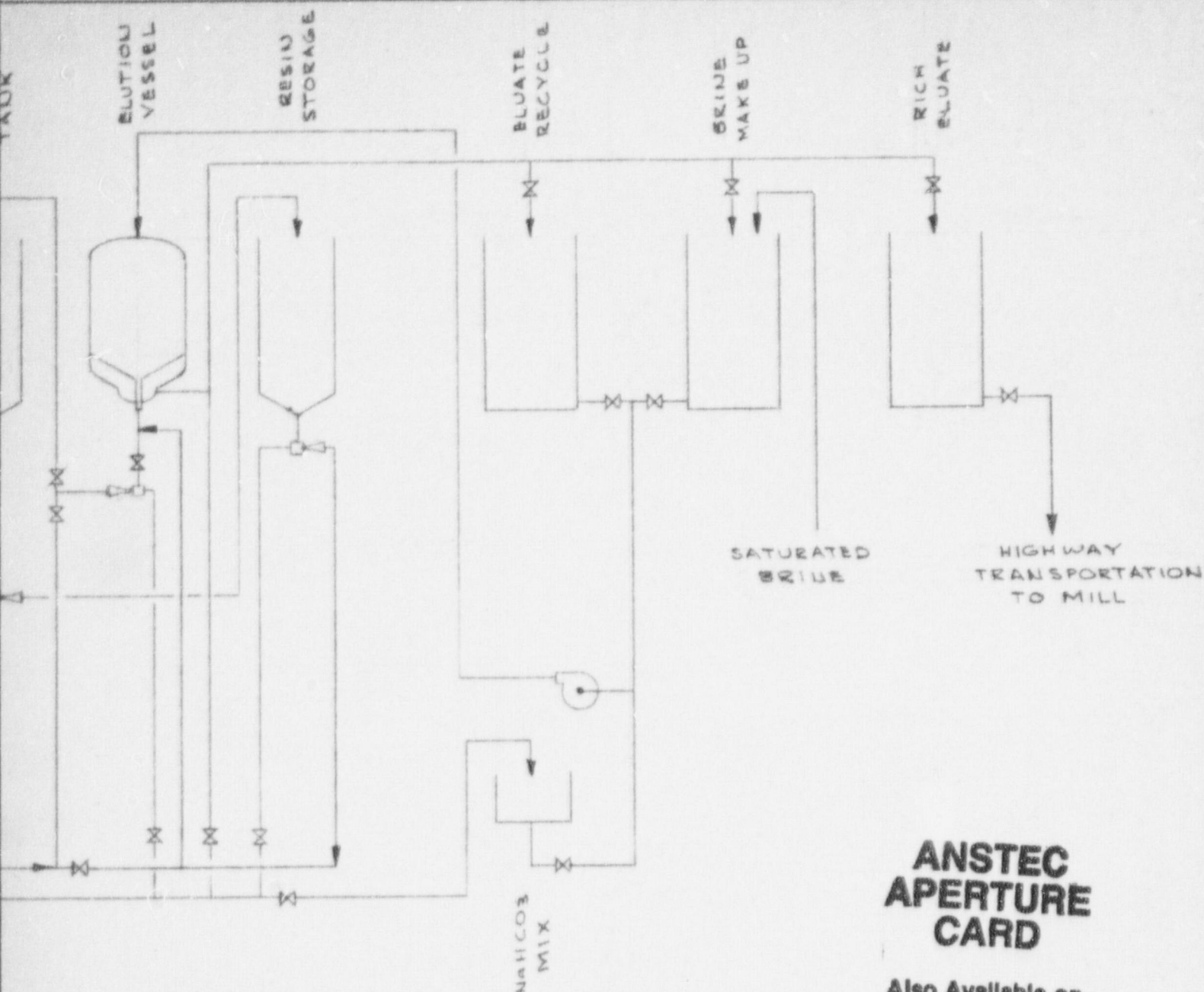
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