NYO-5114

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PROGRESS REPORT

Work completed at Yale on AAA Ore during the period,

April 2 to May 11, 1945

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Earl Miller
Howard Wibbels
Harold Yeager

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Numbering System Used By Yale For Samples

The system is based on the plan of following various elements through the entire process - from digestion to final pure product.

Digestion:	Gangue	2##-DG
	Filtrate	2##-DF
Lead:	Cake	2##-LC
	Filtrate	2##-LF
Barium:	Cake	2##-BC
	Filtrate	2##-BF
Molybdenum:	Cake	2##-MC
	Filtrate	2##-MF

Final solution after boildown and clarification   2##-FS

Extraction

Ether Extract from extractor column	2##-##-EE
Raffinate from extractor column	2##-##-R
Ether extract after washing (in shaker)	2##-##-EE-W#
Ether extract after washing (in column)	2##-##-EE-WC#
Water solution resulting from washing ether extract (in shaker)	2##-##-WW#
Water solution resulting from washing ether extract(in column)	2##-##-WWC#
Water extract from stripper	2##-##-##-WE
Water extract from stripper after washing	2##-##-##-WE-W#(Shaker) 2##-##-##-WE-WC#(Column)
Ether solution resulting from washing water extract from stripper	2##-##-##-EWS#(Shaker) 2##-##-##-EWSC#(Column)
Ether from stripper (recovered solvent)	2##-##-##-RS

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For example:

Sample 215-25-16-WE-W5 refers to the water extract from

    1. washing experiment No. 5 on the water extract from

    2. stripper run No. 16 on ether extract from

    3. extractor run No. 25 on the final solution from

    4. digestion No. 15

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I. Introduction

Because of the possibility that a new plant might be built at MCW for processing a new type of X ore, it was deemed advisable to collect as much data as possible at Yale University where work had been in progress on the process in question for several months. Hence, Earl Miller, Howard Wibbels, and Harold Yeager were sent to Yale University from MCW to both acquaint themselves with the process and also to aid the personnel at Yale University. Upon completion of the contract it is expected that a pilot plant will be built at MCW to carry on the research work on a larger scale than is possible at Yale University.

II. Summary of Work Done

A. Digestion of Ore

The digestion of AAA ore is accomplished by the reaction of the ore with nitric acid at boiling temperatures. This can probably be best accomplished by adding nitric acid to a hot water slurry of the ore. The chief problems in the digestion of the ore are:

1. To obtain a high extraction of X from the ore.
2. To obtain a high extraction of the My from the ore.
3. To digest the material in such a manner that the gangue filtration may be easily accomplished.

X extractions of greater than 99% may be obtained using acid in quantities of 1.3X or greater (1X HNO_3 assumes 7 moles of HNO_3 $\sim$ 1 mole X_3O_8). X extractions using 2X HNO_3 may be as high as 99.9% if the solution is filtered hot and the gangue is thoroughly washed. Low acid digestions such as 1.3X HNO_3 may result in larger fluctuations in X extractions if the ore is likely to vary in X complexes such as X phosphates.

The My extractions are dependent on both the nature of the ore and the methods of digestion and filtration. Large mesh size ore and ore which contains relatively high quantities of sulfate gives poor My extractions. Factors which adversely affect the My extraction are low acid digestion, long digestion periods, and cold filtration.

The filtration of the digestion slurry is very dependent upon temperature of filtration and the acid strength of the digestions. Hot filtrations are much faster and strong acid digestions filter more easily than low acid digestions.

B. Precipitation of Lead

The filtrate from the digestion contains 40-99 percent of the total My in the original ore in addition to the X and other elements present. Because of the radiation hazard, it is advisable

to remove the My from the solution at the earliest possible phase.
Experiments at Yale indicated that the My could be quantitatively
co-precipitated with lead sulfate. Thus, because of the high
value of the My and the radiation hazard, the filtrate from the
digestion is treated with sulfuric acid to precipitate the lead,
a small amount of barium, and My as sulfates. Because of the
high acidity at this point and the relatively high solubility of
lead sulfate in acid solutions, six times the amount of sulfuric
acid, theoretically required to precipitate the lead, is used.
The precipitate generally is crystalline, dense, and very easy
to filter.

Two low acid digestions were made in which part of the filtrate
from the digestion was extracted directly. The purpose of this
was to eliminate the precipitation of excess H_2SO using barium,
precipitating the lead and My in the raffinate with H_2SO_4. These
experiments proved unsatisfactory because lead sulfate of high
activity deposited out on the walls of the extractor during the
extraction.

C. Precipitation of Excess H_2SO_4

The excess sulfuric acid must be removed after the lead precipi-
tation for two reasons:

1. The excess sulfate is harmful to the stainless steel equipment.

2. The excess sulfate will decrease the efficiency of the ether
    extraction.

In order to precipitate the sulfate as $BaSO_4$, $BaCO_3$ was added in
10-15% excess of stoichemetric quantities to the hot solution
containing excess sulfate.

The conditions of precipitating the $BaSO_4$ have a large influence
on its filtration qualities. In the digestions at Yale the fil-
tration rates for filtering $BaSO_4$ ranged from 6 to 42 gallons per
square foot per hour. It is believed that with slow addition of
$BaCO_3$ to a boiling solution containing sulfate, the optimum con-
ditions of obtaining an easily filterable slurry are attained.

D. Precipitation of Molybdenum as Sulfide

In the original flow sheet received from the Manhattan District,
the molybdenum was to be removed as molybdenum sulfide by adding
sodium sulfide to the $BaSO_4$ filtrate. However, the work on pre-
cipitation of molybdenum as the sulfide has been discontinued in
favor of removal of the molybdenum by charcoal. The chief dis-
advantages of the MoS_3 precipitation are as follows:

1. The MoS_3 precipitation does not precipitate sufficient quan-
    tities to insure low Mo goods.

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2. The MoS_3 precipitation also brings down a small amount of X as the sulfide.

3. Emulsion trouble was encountered at Yale after the Mo was removed as the sulfide; identical solutions from which Mo had not been removed did not emulsify.

4. Because the solution had to be adjusted to a pH of 2 (approx.) before the MoS_3 precipitation, the quantity of $NaNO_3$ in solution was too high to allow the addition of $NaNO_3$ in the ore digestion to improve the My extraction.

E. **Addition of Salting Agents**

In most of the work at Yale, $NaNO_3$ was used as a salting agent for the X extraction in ether. However, similar work at 'CW has indicated that $Ca(NO_3)_2$ is better than $NaNO_3$. The chief advantage of using $NaNO_3$ is that the $NaNO_3$ may be added to the original digestion to aid the My extraction; if $Ca(NO_3)_2$ were added, $CaSO_4$ would precipitate with the $PbSO_4$ in the next step in the process.

If it is desirable to use $Ca(NO_3)_2$, and recover the $Ca(NO_3)_2$ for further use, it is necessary to add the $Ca(NO_3)_2$ after the excess H_2SO_4 removal.

If the use of $Ca(NO_3)_2$ is desirable and need not be recovered, the $Ca(NO_3)_2$ could be made in the process after the $PbSO_4$ removal by adding CaO to the filtrate from a strong acid digestion which would be favorable for a good My extraction.

F. **Ether Extraction of X Nitrate**

Two continuous extractors were available at Yale, one a sieve plate, the other a packed column. The extraction efficiencies in both towers were better than 99%. The packed column proved superior to the sieve plate in handling feed solutions which tended to emulsify; solutions which emulsified in the sieve plate column could be run in the packed column by controlling the flow rate. No runs were made to exactly compare the efficiencies of the two towers, but it is felt that the difference is small and a minor factor as compared with emulsion difficulties.

Emulsions could be formed in both columns. Generally they were not extremely difficult to handle. The formation of emulsions seemed to be independent of the character of the preceding precipitations with two exceptions: liquor from the MoS_3 and directly from the lead precipitations formed extremely difficult emulsions which were impossible to break. Some of the emulsions showed a tendency to break when a fine stream of water was sprayed in at the top of the tower. In other cases boildowns of the feed were

found to be very effective in preventing emulsions. The ether
used in the extractions was ordinarily molar in nitric acid.
This prevented the formation of precipitates of phosphates,
etc. in the column and the consequent efficiency loss.

G. Water Washing of Ether Extracts

A continuous spray washer similar to the washing column at MCW
was constructed by H. L. Wibbels. An ordinary water wash of
ether extracts containing Mo was not sufficient to remove the
Mo. Samples of washed extract which were analyzed at MCW for
vitamin indicated that a washing ratio of 10:1 ether extract to
distilled water would reduce the vitamin to 0.5 - 1.0 ppm.
While these values are greater than the limit of 0.5 ppm., it
is believed that a lower washing ratio will wash the vitamin
to less than 0.5 ppm. 3 kg of $XO_2(NO_3)_2$ was prepared from "char-
coalled" and washed ether extract for a shotgun analysis, results
of which are in the latter part of this report.

H. Water Stripping of Washed Ether Extract

A small jet stripping column was made and installed by H. L. Wibbels
to remove the $XO_2(NO_3)_2$ from the ether extract. This apparatus
proved very satisfactory in all respects, i.e., excellent effi-
ciency and rates.

I. De-etherization of Extraction Liquors

Both raffinate and good liquor were de-etherized by heating until
the temperature was above that of boiling water. No brown fumes
were given off in either case until the temperature exceeded 90° C.
Upon further boiling, copious brown fumes were evolved. A large
batch de-etherizer as used in Building 52 (MCW) would be impractical
for this process because of the vigorous reaction; however, a small
continuous de-etherizer such as used in the MCW pilot plant may be
satisfactory.

J. Precipitation of Raffinate

Two de-etherized raffinate solutions were precipitated by adding
a NaOH solution to the boiling raffinate solutions. In both cases
complete precipitation of X was obtained at a pH slightly greater
than seven. The hot filtration of the raffinate was fair (good
clarity but slow rates). From the data obtained at Yale, the
indications are that a sludge pond (as indicated in the original
flow sheet) will not be necessary for the raffinate and that the
filtration may be accomplished to recover the salting agent.

K. Special Molybdenum Experiments

Preliminary experiments have indicated that it is possible to
reduce the molybdenum content of the feed liquor by neutralizing
to an excess acid of about 0.05 N. This causes the formation of
a precipitate which contains phosphate, X, and molybdenum. This
does not seem very promising in view of the loss of X in the
precipitate formed. With this method, the phosphate content of
the ore would be a great factor in the overall efficiency of the
process, higher phosphate contents resulting in increasing losses
of X.

It was found by H. L. Wibbels and E. Miller that it is possible
to remove molybdenum from the ether extract quantitatively by
mixing with finely divided activated charcoal. The adsorption
of the molybdenum is practically instantaneous and there are
indications that it will be possible to rejuvenate the charcoal
at least five times. Likewise, it has been found possible to
remove the X by flushing the charcoal with ether.

L. Miscellaneous Experiments

1. Emulsions

    a. Boildown of Feed Solutions

        Three extractor feed solutions which gave bad emulsions
        in a small laboratory bubbler extractor were concentrated
        to approximately one-third their volumes (X = 120 - 130°C),
        diluted to original volumes, and filtered. On testing
        these boiled-down solutions in the bubbler, no emulsions
        could be formed. A boiled-down solution was similarly
        prepared for the continuous extractor; however, this
        solution was lost and this work was dropped at Yale to
        be continued at MCW if emulsion trouble still persisted.

    b. Charcoal Experiments to Prevent Emulsion

        Two experiments in which the feed solutions were treated
        with activated charcoal and filtered were unsuccessful
        in preventing emulsions.

2. Precipitation of Sulfate as $CaSO_4$ and $BaSO_4$

    It was thought that the sulfate might be precipitated as $CaSO_4$
    in a solution which contained $Ca(NO_3)_2$ as a salting agent.
    This experiment was tried and 40% of the sulfate was removed.
    Since the filtration of $CaSO_4$ is easier than $BaSO_4$, a double
    precipitation of $CaSO_4$ and $BaSO_4$ was tried. The filtration

of both $CaSO_4$ and $BaSO_4$ looked easier on a small scale and will be tried on a larger scale in the MCW pilot plant.

3. My Experiments

a. Roasting of Ore

Under the same conditions of digestion different ores would give a wide variation (40 - 99%) of My recoveries.

It was suggested that a roast of the ore might have a good effect on the My distribution.

An oxidizing roast and a roast with carbon was made on portions of the same ore. The roast was made at the relatively low temperature of 265° C for 18 hours. Subsequent digestions of the roasted ores and a portion of the unroasted ore showed only experimental error variations in My recoveries.

III. Experimental Details

A. Raw Material

The raw material used in Digestions 216-220 (inclusive) was not uniformly mixed and no reliable sample was taken to obtain a complete analysis of the ore.

The X analysis of the ore used is recorded in the data for each digestion.

The analysis of a typical ore gives the following constituents :

X_3O_8 --- $62-72$ %
My   --- $(1.7 \& 2.0) \times 10^{-7}$ g/g
SiO_2 --- $16-19$ %
SO_4 --- $0.5 - 2.5$ %
P_2O_5 --- $0.05 - 0.09$ %
MoO_3 --- 0.50 %
PbO   --- 6.0 %

The screen analysis of the ore wet ground in a ball mill is as follows:

On 100 Mesh	1.8%
On 150 Mesh	6.0%
On 230 Mesh	19.3%
On 325 Mesh	10.9%
Through 325 Mesh	62.0%

FLOW SHEET OF
DIGESTION 216

```
┌─────────────────────┐
│   Ore Digestion     │
│   2X HNO₃           │
│                     │
└─────────────────────┘
            │
            ▼
       ┌─────────┐
       │ Filter  │
       └─────────┘
```

$Ore\ Digestion$ $2X\ HNO_3$

Filter

Gangue

Lead Sulfate
pptn.
and filter
$6.6X\ H_2SO_4$

Lead Cake
$PbSO_4$
$MySO_4$
$BaSO_4$

Part of filtrate to extractor
Extraction 25E

Barium Sulfate
pptn.
and filter
$BaCO_3$

Barium
Sulfate
Cake

Part of filtrate to extractor
Extraction 28E

Molybdenum
Sulfide
pptn. and
filter

Moly. Cake
MoS_3
CoS_2
NiS_2

XS_3?

Salt
Extract

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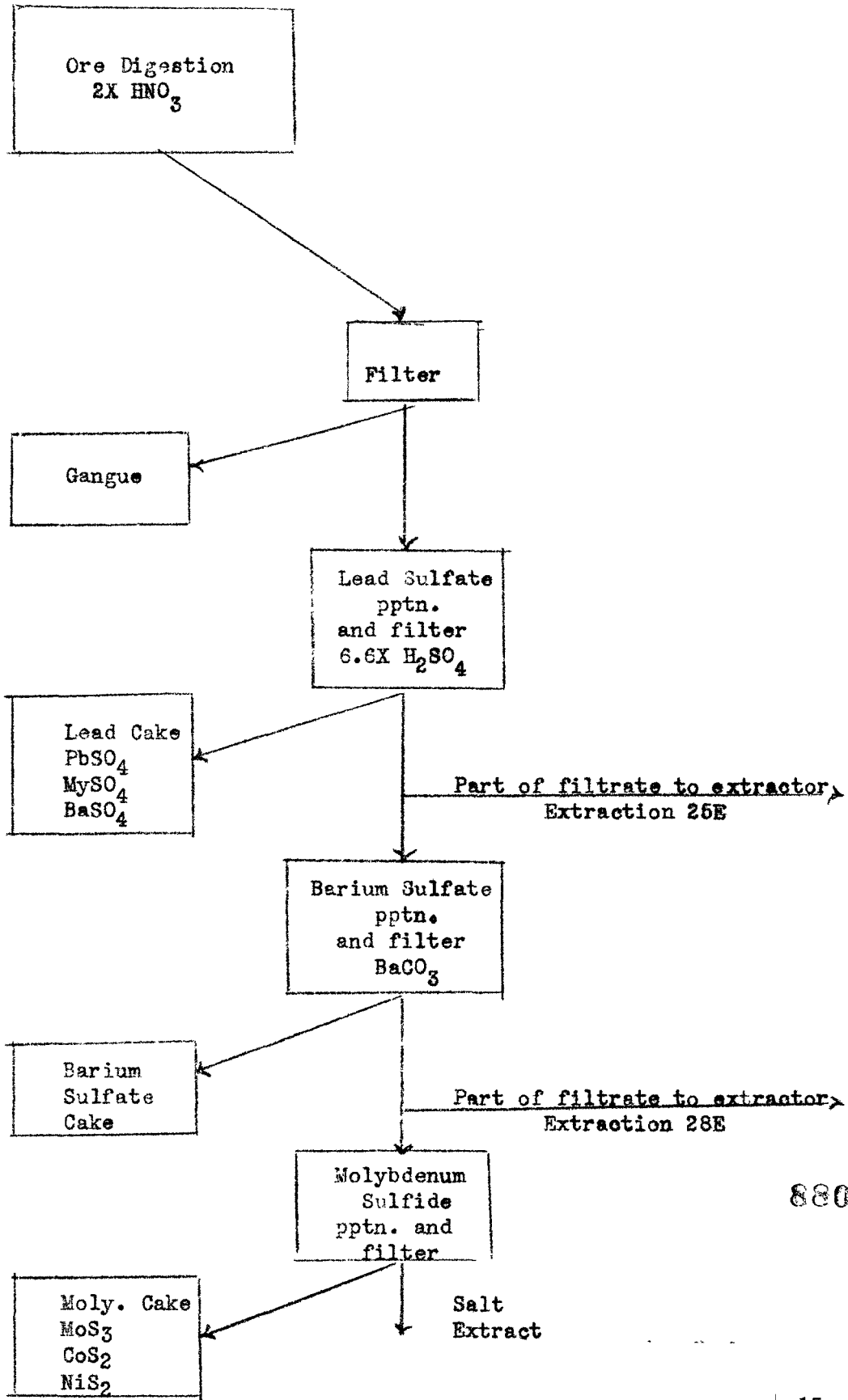
B. Digestion 216

Purpose: To familiarize the Mallinckrodt men with the 45-15 process.

1. Digestion of Ore (2X HNO_3)

126 pounds of wet ore slurry (100 pounds dry weight - 67.5% X_3O_8 dry basic), through 100 mesh, was added to 8.45 gallons of 42° Be HNO_3, diluted with an equal amount of water and heated to 42°C. The ore was added over a period of 23 minutes. The reaction started immediately with the evolution of brown fumes. All visible reaction ceased five minutes after the ore addition was completed. The temperature of the slurry after the addition was 84° C, volume nineteen gallons. The slurry was digested an additional 3.5 hours. At the end of the digestion, the volume of the slurry was brought up to 30.2 gallons by the addition of hot water (58° C).

The hot slurry was filtered through a plate and frame press at a low rate and with some difficulty. (See Engineering B Progress Report). The volume of the filtrate was 31.2 gallons, wash 14 gallons. The dry gangue weighed 15.4 pounds.

The following analyses were obtained:

	Combined filtrate and wash	Dry gangue
Sample	216-DF	216-DG
* XNO_3	0.1883 gms/ml	0.1255 gms/gm
HNO_3	0.13 N	--

X Extraction = 98.4%

* $XNO_3 = YO_2(NO_3)_2$

2. Precipitation of Lead

The combined filtrate and wash from the digestion which had a total volume of 49 gallons was treated with 0.95 gallons of 93% sulfuric acid after control testing. This was 6.6 times the stoichiometric amount of sulfuric acid required. The acid was added to the liquor at room temperature with vigorous stirring.

The slurry was easily filtered through a stainless steel plate and frame press at a rapid rate. The dry weight of the load cake obtained was 5.7 pounds. The volume of the filtrate was 51.2 gallons, wash 5.2 gallons. (See Engineering B for details.)

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XNO_3 in cake (216LC) = 0.000494 gms/gm

X Recovery = 99.97%

Ten gallons of the filtrate was set aside to test the
feasibility of extracting directly without precipitating
the excess sulfate present. (See extraction run 25E.)

3. Precipitation of Excess H_2SO_4

The 46 gallons of filtrate remaining was heated to 82° C.
21.3 pounds of technical grade barium carbonate was added
to the hot solution with stirring over a 30 minute period.
The slurry was digested for two hours at 82-95° C. The hot
slurry filtered fairly well through a plate and frame press.
The total volume of the filtrate and wash was 48.3 gallons.
The dry barium sulfate cake weighed 17.1 pounds. (See
Engineering B for details.) The analyses are tabulated
here.

	Filtrate Analysis	Barium Cake Analysis
Sample	216 BF	216 BC
*XNO_3	0.1385 gms/ml	
MoO_3	0.00018 gms/l	

24.6 gallons of the combined filtrate and wash were set
aside to run directly in the extractor without the sulfide
precipitation and determine whether molybdenum could be re-
moved in the extraction, washing, or stripping steps. (See
extraction run 28E.)

* XNO_3 used in remainder of report is $XO_2(NO_3)_2$.

4. Precipitation of Molybdenum as Sulfide

2.51 pounds of soda ash were added to the 23.7 gallons of
filtrate left from the barium sulfate precipitation to bring
the pH up from 0.68 to 2.48. 0.396 pounds of 60% sodium
sulfide were dissolved in 0.264 gallons of water and the
resulting solution added dropwise over a five-minute period
to the 23.7 gallons of liquor. A precipitate appeared
immediately. The final pH was 2.58.

The slurry was readily filtered through a plate and frame
press. The dry cake weighed 0.154 pounds. (See Engineering
B for details.) Analysis was as follows:

	Filtrate	Sulfide Cake
Sample	216 MF	216 MC
XNO_3		0.3705 gms/gm

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5. **Extraction of Liquors**

    a. **Extraction 25E (Filtrate from Lead Sulfate Pptn.)**

The ten gallons of filtrate from the lead sulfate precipitation was boiled down to about 3 gallons, specific gravity 1.639. The solution was saturated with sodium nitrate, concentration about 1.5 pounds per gallon. The ether was 1N in nitric acid but no analysis was made on the feed solution (calculated 0.93 pounds H_2SO_4 per gallon). This solution emulsified very badly and could not be run in either the sieve plate or the packed column.

    b. **Extraction 28E (Filtrate from Barium Sulfate Pptn.)**

The 24.6 gallons of filtrate from the barium sulfate precipitation was boiled down to a specific gravity of 1.571 and saturated with sodium nitrate (Ca 2.0 pounds per gallon). The ether used was made 1N with 42° Be nitric acid. The analysis of the feed is tabulated here:

XNO_3	0.444 g/ml
HNO_3	0.302 N
MoO_3	0.00049 g/ml

An emulsion formed at the top of the sieve plate tower and gradually worked down the tower. This run was unsuccessful and no samples could be obtained. The Yale people felt that the emulsion was due to the relatively low molybdic oxide content - about 1/3 the usual value for 2X digestions.

    c. **Emulsion Test on the Filtrate from the Molybdenum Sulfide Pptn.**

After the sodium sulfide treatment to precipitate the molybdenum, the filtrate was boiled down. A red precipitate formed during the boildown which was presumed to be sulfur. The precipitate was filtered off and the solution saturated with sodium nitrate.

The Yale laboratory is equipped with a small bubbler setup which represents one of the plates in the sieve plate column. This small bubbler is very effective in ascertaining on a small scale whether or not a given feed will emulsify in the sieve plate column. If an emulsion forms in the bubbler, it will likewise form in the column. The feed solution from the molybdenum sulfide precipitation emulsified so badly that a large run was not attempted. This had been characteristic of all feeds from molybdenum sulfide precipitations tried at Yale.

C. **Digestion 217**

Because trouble was being encountered in washing the molybdenum
complex out of the ether solutions, it was decided to try a low
acid digestion to see what effect this type of digestion would
have on the Mo problem. Also, since the My recovery from a low
acid digestion would be poor, it was decided to try to run the
solution through the extraction column without a removal of the
MySO$_4$. The flow sheet for the process as visualized by this
digestion is as follows:

```
          ┌─────────────────────────────┐
          │   Digestion in 1.3 X HNO₃    │
          └─────────────────────────────┘
                         │
          ┌─────────────────────────────┐
   Gangue │      Gangue Filtration       │
 ┌────────┤                             │
 │        └─────────────────────────────┘
 │                       │
 │        ┌─────────────────────────────┐
 │        │  Concentration and Salting   │
 │        │       of Feed Solution        │
 │        └─────────────────────────────┘
 │                       │
┌──────────┐  Raffinate  ┌──────────────┐
│Re-digestion│◄───────────┤  Extraction  │
│ of Gangue │             └──────────────┘
│  for My   │                    │
└──────────┘             ┌──────────────┐
                         │   Washing     │
                         └──────────────┘
                                │
                         ┌──────────────┐
                         │  Stripping    │
                         └──────────────┘
```

	Feed	Extract	Raffinate
Sample No.	217-26-FS	217-26-EE	217-26-R
XNO_3	429 g/l	234 g/l	0.342 g/l) 2 samples 0.05 g/l)
Sp.G	1.652	1.005	1.315
$NaNO_3$	290 g/l		
HNO_3	0.78 N	0.96 N	0.87 N
MoO_3	1.09 g/l	0.16 g/l	0.69 g/l
My	3.3×10^{-8}		0.4×10^{-8}

	Wash Water	Good Liquor	Stripped Ether
	217-26-WW	217-26-GL	217-26-SE
XNO_3	276.6 g/l	192.7 g/l	0.0114 g/l
Sp.G.	1.268	1.174	0.715
HNO_3	1.65N	0.75N	⌐0.0002N
MoO_3	0.071 g/l	0.105 g/l	N.D.(None detected)
My		N.D.	0.01×10^{-8}

217-26-EE (Ether Extract)(Spectrographic report by N.B.S.)

Ag	⌐0.1 ppm	K	10-25 ppm
Al	⌐10 ppm	Li	0.2-0.5 ppm
As	5-10 ppm	Mg	9
B	2.4 ppm	Mo	100-500
Ca	⌐5	Na	100-500
Cu	5-10	Ni	⌐2
Fe	⌐10	P	50-100
		Fb	20-50
		Rb	20-50
		Si	31*
		V	⌐10

*Reported 67 but corrected for 36 ppm picked up in
porcelain ball mill.

D. **Digestion 218**

Because Digestion 217 was not a 1.3X HNO_3 digestion as was intended,
it was decided to make an actual 1.3X HNO_3 digestion to be carried
through in a manner similar to Digestion 217.

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1. Digestion of Ore

22 pounds of AAA ore (dry basis - 69% X_3O_8) was slurried with
0.53 gallons of water. A nitric acid solution containing
1.39 gallons of 42° Be acid and 0.66 gallons of water was
added to the hot slurry of ore. The time of addition was
22 minutes. The slurry was digested at 90-100° C for 5
hours, filtered hot, and the gangue washed with hot water.

The weight of the gangue obtained was 3.96 pounds (dry
basis).

Analyses:

	Filtrate	Gangue
	218 DF	218 DG
XNO_3	0.4507 g/ml	0.0323 g/g
HNO_3	<0.006N	
MoO_3	0.0052	
My		55×10^{-8} g/g

X Yield = 99.4%
My Yield = 49%

The combined filtrate and wash was concentrated to 12.3
liters and saturated with $NaNO_3$ to be run in the column.

2. Extraction (27E)

The extraction was made in the sieve plate column. A slight
emulsion formed at the beginning of the run; however, later
in the run the emulsion gave no trouble. A white precipitate
formed on the walls and on the plates. This precipitate was
similar to the one found in 26E. ($PbSO_4$ and $MySO_4$).

Extraction Data:

Feed Rate	70 cc/min
Solvent Rate	140 cc/min
Washing Ratio	1/10 (water:ether)
Acid in Ether	1N
Efficiency of Extraction	99.96%

Analyses:

	Feed	Extract	Raffinate
	218-FS	218-27-EE	218-27E-R
XNO_3	489.6 g/l	261.2 g/l	0.247 g/l
Sp.G.	1.615	1.008	1.270
HNO_3	0.0112N	0.37N	1.08N
MoO_3	0.45 g/l	0.00335 g/l	0.61 g/l

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Spectrographic Analysis of MCW (ppm)

	Wash Water	Washed Extract
Vitamin	>10 (Est. 30)	0.74
Cd	>WE	<WW
Fe	low	low
Pb	>little	little
Mn	very low	very low
Mo	about 60	<10
Ag	<0.2	>4
Na	some	none
Ni, Cr	<10	<10
Mg	20	20
P	>WE	
Co	~10	~10

E. Digestion 219 (1.3X HNO_3)

Digestion 218 was successful in keeping the Mo in the raffinate; hence, it was decided to make a 100-pound digestion to gather both engineering data and also to prove that a 1.3X HNO_3 digestion is successful in removing Mo.

1. Digestion of Ore

An ore slurry of 6.3 gallons was made with 100 pounds of dry ore. The weight of the wet slurry was 141.6 pounds.

The ore slurry was heated to 80° C and 7.2 gallons of nitric acid solution containing 3.51 gallons of 40° Be HNO_3 was added to the hot slurry over a period of 10 minutes. The digestion was made in the 100-gallon tank. Visible reaction started immediately upon the addition of acid and ceased about 10 minutes after the last of the acid was added. It was difficult to determine the amount of foaming in the tank because of the NO_2 fumes, but it was estimated that there was only about 3 or 4 inches of foam above the liquor while the acid was being added.

Samples were taken for X and My every 30 minutes after the digestion was started. The slurry was digested for 3 hours at 85-100° C.

The slurry filtered very poorly through the Sperry Filter press and the Oliver Filter. (See Engineering B for details.)

After 10.5 gallons of clear filtrate had been obtained, this amount was set aside to be treated with H_2SO_4. The remainder of the slurry was filtered and 7.8 gallons of filtrate was obtained. The first filtrate of 10.5 gallons was sampled and labelled 219-DF.

680   023

Because of the difficulty encountered in filtering the gangue
and also in order to expedite the remaining operations, it
was decided not to re-slurry and wash the gangue to remove
the remaining XNO_3. It was assumed that the small samples
taken for My and X analyses would suffice to determine the
X recovery. Also, it was assumed that the weight of gangue
obtained after washing free of X would be the same as that
obtained in Digestion 218; e.i., 3.9 pounds of dry gangue
per 22 pounds of dry ore.

Therefore, the weight of gangue obtained from Digestion 219
was assumed to be 17.74 lbs.

Analyses:

Gangue Analysis

Sample No.	Digestion Time (Hrs)	My (g/g)	XNO_3 (g/g)
219-DG-1	0.5		0.0076
219-DG-2	1.0		
219-DG-3	1.5		0.00512
219-DG-4	2.0		
219-DG-5	2.83	34.0×10^{-8}	0.0305
219-DG-6	7.0		0.0324

Filtrate Analysis

Sample No.	219-DF
Sp. G.	1.401
XNO_3	0.4074 g/ml
HNO_3	0.03N
PbO	0.0154 g/ml

2. Precipitation of Lead

a. First Portion of 219-DF

The lead in the first filtrate from 217-DF (10.5 gallons)
was precipitated as $PbSO_4$ by adding 0.221 gallons of 66°
Be H_2SO_4. This quantity of H_2SO_4 is 5.4 times the amount
of H_2SO_4 equivalent to the PbO found in the solution.

The $PbSO_4$ slurry was filtered through the Oliver Filter
and a table-top Buchner funnel. (See Engineering B for
details on filtration.) The cake was not sampled or
weighed because of losses and contamination in using
the Oliver Filter.

Ten gallons of clear filtrate was obtained from the
$PbSO_4$ filtration.

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Analysis of Filtrate

Sample No.	219-LF
XNO_3	0.3982 g/ml
MoO_3	0.00034 g/ml

b. Second Portion of 219-DF

7.8 gallons of 219-DF (Second Portion) was treated with 0.18 gallons of H_2SO_4 to precipitate the lead as $PbSO_4$. The slurry was filtered through a table-top Buchner funnel. No filtration data or samples were taken.

3. Precipitation of Excess H_2SO_4

a. First Portion of 219-LF

Ten gallons of 219-LF (First Portion) at 82.5° C was treated with 6.6 pounds of $BaCO_3$ and digested for 1 hour at 80-90° C.

The solution was allowed to settle for 35 hours and was filtered by decantation through a Buchner funnel.

No samples and no filtration data were taken.

The filtrate was then concentrated to a specific gravity of about 1.6 and was saturated with $NaNO_3$ to be run in the extraction column. See Extraction Run 29-E.

b. Second Portion of 219-LF

Because the feed solution (219-FS First Portion) emulsified in the sieve plate column (29-E) and also because it had been shown that concentration, dilution, and filtration of a feed solution tended to eliminate emulsion trouble, it was decided to concentrate the second portion of Digestion 219-LF after the $BaCO_3$ had been added to see if the material could be run in the column after boil-down.

7.8 gallons of 219-LF (Second Portion) was heated to 82° C and 4.9 pounds of $BaCO_3$ was added with stirring to precipitate the excess sulfate. After the $BaCO_3$ had been added, the solution was concentrated in one of the 30-gallon tubs to a thick paste over a period of about 5 hours. The temperature at the end of the heating period was about 120° C, though the measurement of the temperature was meaningless because the solution was not boiling. The solution was diluted to a specific gravity of about 1.6 and was filtered through a table-top funnel. The precipitate of $BaSO_4$ plus material boiled out of solution

880   025

was brown in color. It was then intended that the filtrate be saturated with $NaNO_3$ to be run in the column, but the solution was lost when the container was broken.

4. **Extraction (29-E)**

The feed solution from the 219-BF (First Portion) was tried in the bubbler and an emulsion was indicated. However, an attempt was made to run the solution in the sieve plate column. A bad emulsion formed and no samples could be taken.

Extraction Data:

Acid in Ether	1N
Feed Rate Tried	70 cc/min*
Solvent Rate Tried	140 cc/min

Analysis:

Feed	219-FS
XNO_3	606.1 g/l
Sp. G.	1.695
$NaNO_3$	saturated
HNO_3	0.005N
MoO_3	0.516 g/l

* The sieve-plate column can be run at only 140:70 rates in order to control the interfaces.

In order to determine the Mo distribution from Digestion 219, a counter-current batchwise shakeout of 219-FS was made.

Results: (Extract)

XNO_3	316 g/l
Sp. G.	1.054
MoO_3	0.0064 g/l

This represents about 1/34 the MoO_3 found in the extract of Digestion 217 (1.8 x HNO_3).

F. **Digestion 220 (2X HNO_3 + 20% $NaNO_3$)**

Purpose : To try 20% $NaNO_3$ to improve My removal from gangue, also to try various experiments on the same liquors for Mo removal.

1. **Digestion of Ore**

66 pounds of AAA ore (69% X_3O_8 dry basis) and 13.2 pounds of $NaNO_3$ were slurried with 3.33 gallons of water and heated to 50° C.

Flow Sheet For
Digestion 220
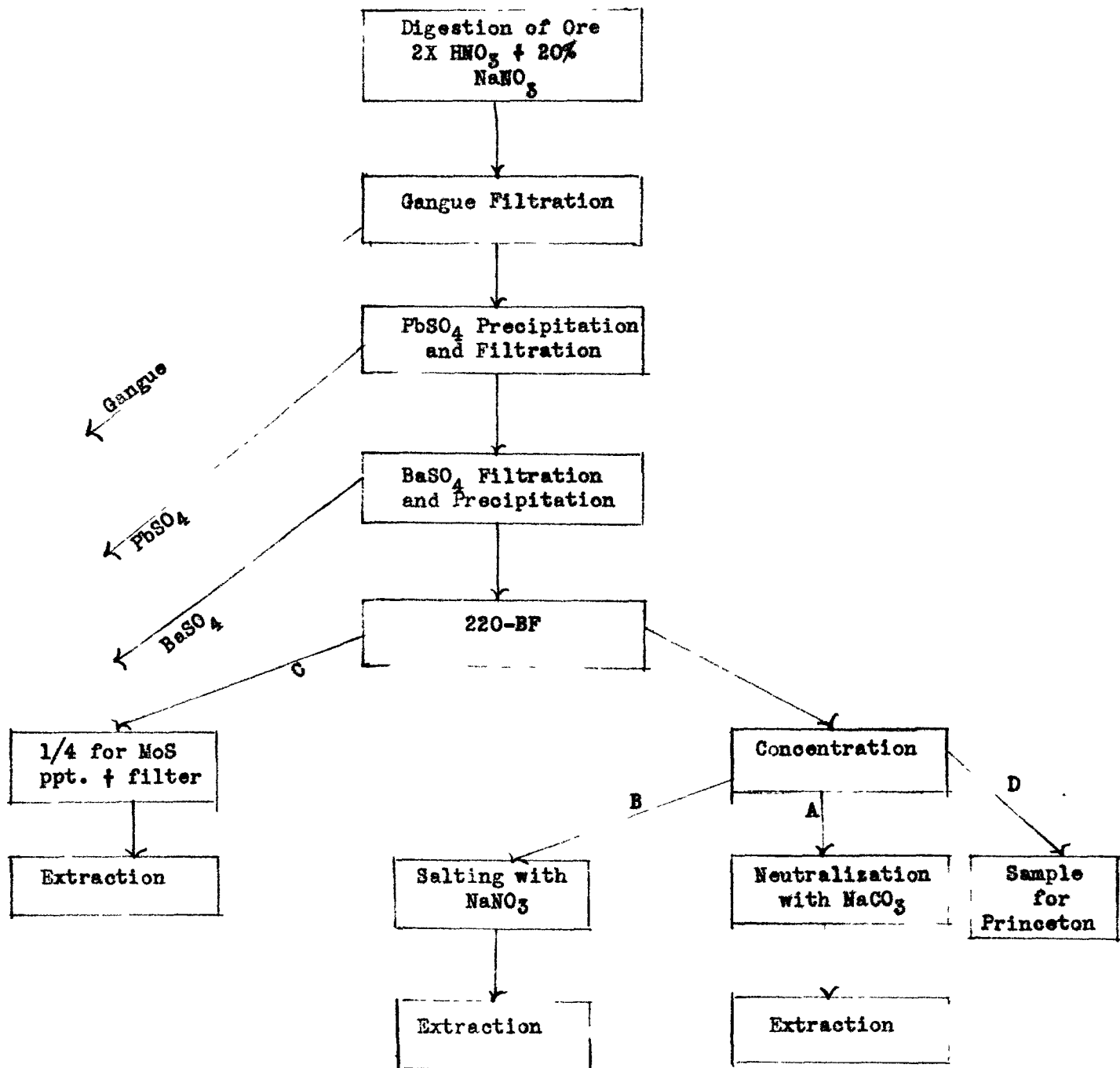
880 027

3.33 gallons of 40° Be nitric acid was slowly added to the hot slurry and the slurry was digested at 90-100° C for 1 1/2 hours. At this time it was discovered that only 1X of HNO_3 had been added; hence, 4.02 gallons of 36° Be HNO_3 was added to the slurry. There was little evolution of nitrous fumes upon the second addition of acid. Digestion at 90-100° C was continued until the period of time from the beginning of the acid addition was three hours.

The slurry was then diluted to 12 1/2 gallons with hot water and a small sample of the slurry was filtered and washed with hot water to obtain the My and X recovery.

The remainder of the slurry was filtered and washed with hot water in the Nutsche Filters.

The total volume of filtrate was 28 1/4 gallons and the weight of the wet gangue was 39 pounds.

Analyses:

	Gangue	Filtrate
Sample No.	220-DC	220-DF
XNO_3	0.0324 g/g	0.2478 g/ml
My	39.0 x 10^{-8} My/g	
HNO_3		0.51 N
PbO		0.0138 g/ml

X Yield = 99.5%
My Yield = 67.8%

2. Precipitation of Lead

0.528 gallons of 66° Be H_2SO_4 was added to the 28 1/4 gallons of filtrate from the gangue filtration to precipitate the lead. Based on the lead analysis of the gangue filtrate, 5.3X the stoichemetric quantity of H_2SO_4 was required to precipitate the lead.

The solution was then filtered by decantation through a Buchner funnel. No data was taken on the filtration.

Analysis:

Filtrate

Sample No.	220-LF
MoO_3	0.00114 g/ml

880 028

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3. Precipitation of Excess H₂SO₄

The filtrate from the PbSO₄ removal was heated to 80-90° C and 14.75 pounds of BaCO₃ was added to the solution to precipitate the excess sulfate.

The solution was digested for about two hours and filtered by decantation through a Buchner funnel.

The total volume of filtrate and wash after the BaSO₄ filtration was 27.8 gallons. 5.7 gallons of this filtrate was set aside to be treated with Na₂ S. The remainder of the solution was concentrated to a volume of 11 1/4 gallons.

4. Precipitation of Molybdenum

From the analysis of 220-LF it was calculated that 2.01 pounds of Na₂ S (60%) would be required to precipitate the Mo. This amount of Na₂ S was dissolved in 1.16 gallons of water.

1.9 pounds of Na₂CO₃ was slowly added to the solution while stirring. The Na₂ S made the solution so basic that it became necessary to add nitric acid to the solution to prevent the precipitation of X compounds. A total of 940 cc of 36° Be nitric acid diluted 1:1 with water was used. The final pH of the solution was 1.42.

The sulfide precipitate was then filtered through a Nutsche filter. No filtration data and no samples of the cake were taken.

The filtrate from the sulfide precipitation was then concentrated to be run in the packed column. This feed solution was labeled 220-C. (See extraction 33E).

5. Disposition of Remainder of 220-BF

   a. 3 3/4 gallons of the 11 1/4 gallons of concentrated liquor from the BaSO₄ filtration was sent to Princeton to be used in some Molybdenum experiments. (220-D)

   b. 3 3/4 gallons of the concentrated liquor was saturated with NaNO₃ to be run in the packed column. This solution was labeled 220-B (see 32-E).

   c. The concentrated solution from the BaSO₄ filtration was tested for excess HNO₃ and found to be 0.98N. The amount of soda ash required to neutralize this acid was 1.635 pounds. This amount of soda ash was slowly added

to the remaining 3 3/4 gallons of the concentrated 220-BF. The solution was hot and being stirred while the soda ash was being added. A yellow precipitate formed.

The neutralized solution was then filtered. No filtration data and no samples were taken for analyses. The filtrate was labeled 220-A and was run in the packed column. (See 30-E and 31-E.)

6. **Extraction of 220-A FS (30-E and 31-E)**

a. **Extraction Run 30-E**

An attempt was made to run 220-A in the sieve plate column. However, the solution emulsified and a run could not be made.

b. **Extraction Run 31-E**

The packed column used in all of the previous experiments at Yale was packed with 7 mm rings. There was considerable channelling in this column. These 7 mm rings were removed before Run 31-E and replaced with 6 mm rings. Also, when the 6 mm rings were packed in the column, the free space between the rings was reduced by tapping the flanges between the sections with a wrench. The height of packing with the 6 mm rings was 9 1/2 feet. (19 sections) as compared with 13 1/2 feet (27 sections) with the 7 mm rings.

220-A was then tried in the packed column. At the start of the run the feed rate was 50 cc/min and the solvent rate was 100 cc/min. At this rate there was no flooding and no emulsion. The rate was then increased to 60:120 cc/min (feed:solvent). At this rate there was slight flooding, and an emulsion rose about 3 inches above the top of the packing. The rate was then reduced to 55:110 cc/min. At this rate there was no flooding and only about 1 inch of emulsion above the top of the rings. The rate was then reduced to 102:47.2 cc/min. and the run was completed at this rate with no further trouble

Extraction Data:

Feed Rate	47.2 cc/min
Solvent Rate	102 cc/min
Acid in Ether	1.22 N
Efficiency of Extraction	99.77%

<u>Analyses:</u>

	Feed	Extract	Raffinate
Sample No.	220-A	220-A-31-EE	220-A-31-ER
Sp.G.	1.648	1.007	1.287
XNO_3	506.5 g/l	242.3 g/l	1.4 g/l
HNO_3	0.15 N	0.80N	0.98N
$NaNO_3$	saturated	0.80N	0.98N
MoO_3	0.45 g/l	0.052 g/l	0.53 g/l
P_2O_5	0.41 g/l		
Si			

7. <u>Extraction of 220-B-FS (Extraction 32-E)</u>

Solution 220-B was extracted in the packed column.

The feed rate was started at 55 cc/min with a solvent rate of 110 cc/min. There was considerable emulsion and flooding. The rate was reduced to 50:100 cc/min, 45:90 cc/min., and finally to 41.5 - 88.6 cc/min at which rates the run was completed.

<u>Extraction Data:</u>

Feed Rate	41.5 cc/min
Ether Rate	88.6 cc/min
Acid in Ether	1.03 N
Efficiency of Extraction	99.55%

<u>Analysis:</u>

	Feed	Extract	Raffinate
	220-B	220-B-32-EE	220-B-32E-R
Sp.G.	1.609	1.001	1.270
XNO_3	457 g/l	218.7 g/l	2.240 g/l
HNO_3	0.76 N	1.03 N	0.95N
MoO_3	1.83 g/l	0.222 g/l	1.0 g/l
SiO_2	0.14 g/l		
P_2O_5	0.375 g/l		

The extract from 220 A (neutralized feed) had about 1/5 the amount of Mo in the extract from 220 B (not neutralized).

8. <u>Extraction of 220 C-FS (Extraction 33F)</u>

Extraction made in packed tower. This is the feed from which the Mo had been removed by Na_2S.

860 031

Feed rate = 70 cc/min.
Solvent rate = 140 cc/min. (1.09 N in HNO_3)
Extraction efficiency = 99.8%

Extraction Data:

No emulsions were formed which was contrary to previous results of feed from which Mo had been removed by Na_2S. It appeared that most of the extraction was taking place in the upper 1/3 of the tower.

Analysis:

	Feed	Extract	Raffinate
Sp. G.	1.512	0.880	1.340
XNO_3	238 g/l	120 g/l	0.55 g/l
MoO_3	0.026 g/l	.0014 g/l	0.034 g/l
HNO_3	0.02 N	0.79 N	0.78 N
$NaNO_3$	380 g/l		
SiO_2	0.140 g/l		
P_2O_5	0.025 g/l		

G.   **1000 Pound Uniform AAA Ore Batch**

Previous digestion results were difficult to correlate because of using various lots of A A ore which did not have complete analysis. It was therefore decided to get a large uniform ore batch on which to perform our next series of digestion experiments.

A 1000 pounds of dry ore was wet milled (ball mill) at American Cyanamid of Stamford, Connecticut. It was received at Yale in five 10 gallon clamp-top drums and one 25 gallon glass-lined drum. It was tested as it was milled to all pass through 100 mesh.

Since the milled ore slurry was not uniformly mixed, we mixed the complete batch (1500 pounds wet) in a 90 gallon stainless steel tank using two large Lightnin mixers and one small mixer. While stirring, six samples were taken in various parts of the slurry for X and moisture analysis and then the well-stirred mixture was subdivided into 10 and 30 kg. batches (dry basis).

Screen Analysis: (Wet, uniformly mixed ore slurry)

On 100 mesh	0.5%
On 150 mesh	1.5%
On 250 mesh	14.1%
On 325 mesh	8.0%
Thru 325 mesh	75.9%

880   032

<u>Chemical Analysis:</u>   (dry basis) (Slurry = 31% H_2O)

X_3O_8	61.91%
SiO_2	19.7%
P_2O_5	0.21%
MoO_3	0.51%
PbO	6.9%
My (Calc.)	1.74×10^{-7} g/g
My (Analyt)	2.12×10^{-7} g/g

A small sample of the dry ore before milling was seen. It contained considerable fine dark gray heavy material and also larger particles up to 3/8 inch which varied in color from black to a bright yellow orange. The orange pieces were quite soft and very difficult to mill. It was also noted that this ore slurry was a lighter gray color than previous batches.

H.   Digestion 221

<u>Purpose:</u>   This digestion (2 hours with 2X HNO_3 + 20% $NaNO_3$) was made to conform to the tentative process drawn up to obtain cost estimates on equipment. It is also the type of digestion recommended by Yale to give satisfactory My and X recovery from gangue.

Complete data through "shotgun" test is included in this digestion.

1.   <u>Digestion of Ore</u>

A portion of the 1000 pound uniform ore slurry equivalent to 22 pounds of dry ore was mixed with 4.4 pounds of $NaNO_3$. The mixture was heated to 55° C in a 6.5 gallon stainless steel tank with stirring and 2.43 gallons of 36° Be HNO_3 was added over a 21 minute period.

There was the normal short induction period before brown fumes came off. There was a maximum of about 3 inches of foam with brown fumes after about 2/3 of the acid was added. After this point, acid could be added as rapidly as desired.

Volume before acid addition	2.64 gallons
Volume after acid addition	4.75 gallons

The 2 hour digestion was made at 92-106° C.

Throughout this digestion, samples of the digestion liquor were taken at the following designated times for My and X analysis:

880   033

(The samples were filtered hot on a Buchner and all were washed with the same amounts of hot water.)

Sample	Time of a Digestion	Analysis	
		My % in Gangue	XNO_3 % in Gangue
221-DG-1	21 min.	1.2	0.0029
221-DG-2	51 min.	1.7	0.00424
221-DG-3	61 min.	1.7	0.00757
221-DG-4	121 min.	1.2	0.0218
221-DG-5[b]	121 min.	1.2	
221-DG-6[c]	186 min.	9.2	0.037

Notes:

- a. Zero digestion time is taken when acid addition is started.

- b. Sample four filtered in 1 minute 40 seconds at 100° C. Sample 5 was boiled down to 130° C, diluted back to original volume (same as 4) and filtered in 1 minute at 100° C.

- c. This sample was taken 67 minutes after completion of digestion-temperature approximately 60° C. This would simulate filtration time in plant.

On completion of the two-hour digestion period, the digestion slurry was diluted to 4.75 gallons (original volume after all acid added) and the greatest part of it was filtered through the Oliver at fairly good rates (see Engineering B report). The remainder of the slurry and the filtrate from the Oliver was clarified by filtering through a table top Buchner pre-coated with filter cel.

The gangue was reslurried with two gallons of water, heated to 70° C and filtered (see Engineering B report). Total volume of wash and filtrate = 6.0 gallons. Weight of gangue not obtained but by calculation from 100 g beaker digestions it was estimated at 4.54 pounds (dry).

Analysis of 221-DF (from above 6 gallons)

PbO	Samples lost
HNO_3	0.74 N
ANO_3	Samples lost

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2. Precipitation of Lead: (See Engineering B for filtration data)

0.132 gallons of 66° Be H_2SO_4 was required to completely pre-cipitate the lead, representing 3.44 x stoichiometric (from weight of LC). The precipitation was done at room tempera-ture with very good agitation. The acid was added fairly rapidly and gave a precipitate which filtered easily but difficult to obtain an absolutely clear filtrate. Cake washed by displacement.

Analysis of 221-LC: Analysis of 221-LF:

Total wet weight = 1.81 pounds
Total dry weight = 1.36 pounds   Vol. = 7.07 gallons.
XNO_3 = 0.0100gm/gm
H_2O = 24.8%

3. Precipitation of Excess H_2SO_4

The 7.07 gallons of LF was heated to 84° C and 3.97 pounds of $BaCO_3$ was added during a three-minute period with very slight foaming. (3.97 pounds $BaCO_3$ represents a 33.6% ex-cess which is at least twice too much).

The $BaSO_4$ precipitate was digested two hours at 75-84° C. Filtration was attempted on the Oliver (see Engineering B report) and clarified in a Buchner with some difficulty. The cake was washed with two liters of cold water.

Analysis of 221 BC

Total wet weight	3.75 pounds
Total dry weight	3.26 pounds
XNO_3	0.0010 gms/gm
My	0.8×10^{-8} gms/gm
H_2O	13.15%

The BF was evaporated to 2.64 gallons. It crystallized at room temperature so it was diluted with two liters of water. Crystals still formed, so water was added until total volume was 4.1 gallons, crystals still formed. These crystals were identified as $BaNO_3$. The BF was not saturated with $NaNO_3$

4. Extraction (34 E) (Packed Tower - 1 inch x 9 1/2 feet 6 mm rings)

Analysis of 221-FS

Sp. G.	1.584
XNO_3	493 g/l
HNO_3	0.90 N
$NaNO_3$	104 g/l
MoO_3	1.525 g/l
SiO_2	0.13 g/l
P_2O_5	0.124 g/l

The solvent was 1N with HNO_3.

Extraction Data:

Feed rate = 60 cc/min. (jet) Wash ratio = $\dfrac{1}{12}\ \dfrac{(H_2O)}{(Et_2O)}$

Solvent rate = 120 cc/min. (jet) Stripping ratio = $\dfrac{1}{1.7}\dfrac{(H_2O)}{(Et_2O)}$

There was no emulsion or flooding trouble at these rates.
The extraction went smoothly. Flooding rates were 70:140.

The extract from this run was charcoaled, filtered, washed
and stripped for the purpose of a shotgun sample. Details
of this charcoaling can be found in this report under III-P
Preparation of Shotgun Sample.

Efficiency of extraction = 99.8%

Test	Extract*	Charcoalled Extract (not washed)	Good Liquor	Raffinate
Sp.G	1.028	-	1.177	1.204
XNO_3	260 g/l	-	-	1.49 g/l
HNO_3	0.95 N	-	0.87 N	1.24 N
MoO_3	0.034 g/l	lost	-	-

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(Spec. at Mallinckrodt)

Ag	<2 ppm	<2 ppm	<2 ppm
Co	<10 ppm	<10 ppm	<10 ppm
Cr	<10 ppm	<10 ppm	<10 ppm
Fe	14 ppm	16 ppm	<10 ppm
Mg	8.4 ppm	2.4 ppm	2.0 ppm
Mn	1.8 ppm	2.0 ppm	1.5 ppm
Mo	trace	none	none
Ni	<10 ppm	<10 ppm	<10 ppm
Na	trace	faint	faint
Pb	faint	faint	trace
Si	trace	trace	trace
B	4.7 ppm	6.3	1.2

* No analyses were run on the washed extract.

5. **De-etherization and Precipitation of Raffinate**

The Area Engineer's flow sheet indicates a sludge pond. This
experiment was performed to see if we could precipitate X
and other metals using caustic. We could then filter off

the insoluble sodium salts with the possibility of recovering $NaNO_3$ from the filtrate or $Ca(NO_3)_2$, providing CaO is used to neutralize the raffinate and no $NaNO_3$ is used during digestion or for salting the feed.

Volume of raffinate to de-etherize was 1.98 gallons. A steam coil was used for de-etherization. The ether evaporated off very nicely over about a five-minute period. When the temperature reached 95° C, brown fumes came off and there was approximately eight inches of foam. When steam was turned off, there was a continued auto-reaction with evolution of brown fumes and foaming for several minutes. After twelve minutes, the boiling with the steam coil was stopped (maximum temperature was 106° C).

The de-etherized raffinate was diluted to nine liters with water and neutralized to a pH of 7.3 with 20% NaOH. The precipitate was filtered successfully.

There was 18 grams of dry solids for 100 cc of filtrate. Details of filtration data can be found in Engineering B report.

6. De-etherization and Boildown of Good Liquor

(See section III-P -Preparation of Shotgun Sample)

I. Digestion 222

Purpose: This 2.5X HNO_3 2 1/2 hour digestion with no $NaNO_3$ was tried in an effort to see if the extra 0.5X HNO_3 would be equivalent to 20% $NaNO_3$ in My recovery. If the feed turned out too acidic it was to be neutralized with CaO.

Complete data on this digestion through "shotgun" test is included.

1. Digestion of Ore

22 pounds (dry basis) of the ore slurry from the 1000 pound uniform ore batch was heated to 50° C and 2.99 gallons of 36° Be HNO_3 was added over an 18 minute period.

Reaction was made in a 6.5 gallon stainless steel tank efficiently agitated with a small Lightnin mixer.

Volume before acid addition	2.64 gallons
Volume after acid addition	5.28 gallons
Volume after digestion	4.5 gallons

There was a maximum of approximately four inches of foam with brown fumes after a little over half the acid was added.

After two-thirds of the acid was in, it could be added as rapidly as possible with no foaming.

The 2 1/3 hour digestion was made at a temperature of 75-85°C.

At various times throughout the digestion samples of the digestion slurry were taken, filtered hot, and washed thoroughly with the same volumes of hot water for the purpose of My and X analysis to determine optimum digestion time.

Results are in the following table:

Samples	Time of a Digestion	My Percent in Gangue
222-DG-1	20 min.	0.676
222-DG-2	50 min.	0.99
222-DG-3[b]	140 min.	0.52
222-DG-4[c]	200 min.	1.09

Notes:

a. Zero digestion time is taken when acid addition is started.
b. Same sample volume same as 221 DG 5; same filter media and pressure. Filtration rate = 1 min. 15 sec.

c. This sample represents time slurry would stand while filtering in plant. Temperature was 58° C.

The digestion was stopped after 2 1/3 hours and filtration in the Oliver was tried with fair success. (See Engineering B report.) The remainder of the slurry and the filtrate from the Oliver was clarified on table top Buchners.

The gangue was reslurried with two gallons of water heated to 60° C and filtered.

Combined volume of wash and filtrate was seven gallons. Weight of gangue was not obtained, but from beaker experiments of same ore it was estimated to be 4 pounds (dry). Analysis of 222DF (combined with wash)

XNO_3 0.304 gms XNO_3/ml
HNO_3 1.45 N

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2. Precipitation of Lead

0.171 gallons of 66° Be H_2SO_4 was added rapidly to the above seven gallons of DF with efficient stirring at room temperature. (The H_2SO_4 was at least 0.04 gallons excess due to a miscalculation.)

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The filtration on a table top Buchner was rapid but it was very difficult to obtain a clear filtrate due to the fineness of the $PbSO_4$ crystals. Slower addition of H_2SO_4 is observed by the Yale personnel to give a precipitate of better filtering qualities. Cake was washed with cold water. Volume of filtrate and wash was 7.8 gallons.

3. **Precipitation of Excess H_2SO_4**

The 7.8 gallons of LF was heated to boiling (steam coil) and 5.08 pounds of $BaCO_3$ was added during a nine-minute period. A control test indicated no $SO_4^=$ and an excess of Ba^{++}.

After digesting one hour at boiling, the filtration of the slurry was tested with good results (Engineering B Report). It was digested one-half hour more and filtration on Oliver was tried with good results (see Engineering B report). The filtrate was clarified and the remainder of the $BaSO_4$ was filtered through a table top Buchner. The rapid filtration with clear filtrate from the $BaSO_4$ slurry is attributed to the fact that we boiled the LF while adding the $BaCO_3$ and also boiled during the digestion, thus giving a better precipitate for filtering.

Analyses of 222 BC ÷ 222-BC-3- 0.0011 g XNO_3/g
         222-BC-4- 0.0023 g XNO_3/g
         My - 0.60×10^{-8} gms/gm

No analysis of 222-BF - volume was 4.85 gallons, which was boiled down with no salting to a 1.506 specific gravity.

4. **Extraction (35-E)**   (Packed Tower)   (1 inch x 9 1/2 feet - 6 mm rings)

Feed Analysis:

Sp. G.	1.506
XNO_3	464 g/1
HNO_3	1.7 N
MoO_3	2.62 gms/1
SiO_2	0.14 gms/1
P_2O_5	0.115 g/1
$NaNO_3$	82 g/1

The solvent was 1N with HNO_3'.

Extraction Data:

Feed rate	70 cc/min	Wash water	$\frac{1 \ (H_2O)(Jet)}{12 (Et_2O)}$
Solvent rate	140 cc/min	Stripping ratio	$\frac{1 \ (H_2O)(Jet)}{1.7 \ (Et_2O)}$

No emulsion or flooding trouble was observed at these rates.

The extract from this run was charcoalled, washed, and stripped to be combined with 221-34EGL for a shotgun test. Details of this can be found under III P- (Preparation of Shotgun Sample).

Efficiency of Extraction = 99.3%

Test	Extract	Charcoalled* Extract (unwashed)	Good Liquor	Raffinate
Sp.G	1.050	--	1.224	1.125
NO_3	266 g/l	--		3.46 g/l
HNO_3	1.20	--		1.65 N
MoO_3		0.0012 g/l		

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(Spec. at Mallinckrodt)

Ag	<2 ppm	<2 ppm	none
Co	<10 ppm	<10 ppm	<10 ppm
Cr	<10 ppm	<10 ppm	<10 ppm
Fe	<10 ppm	<10 ppm	<10 ppm
Mg	20 ppm	<2.0 ppm	<2 ppm
Mn	2.3 ppm	1.7 ppm	1.7 ppm
Mo	>trace	none	none
Ni	<10 ppm	<10 ppm	<10 ppm
Na	faint	faint	none
Pb	trace	trace	none
Si	trace	trace	trace
B	4.8	5.9	1.5

*No analysis run on charcoalled, washed extract.

5. De-etherization and Precipitation of Raffinate

Raffinate volume was 7.5 liters. Ether boiled off very nicely using a steam coil. When temperature reached 92° C after ten minutes, an auto-reaction started with considerable foaming and brown fumes which would continue several minutes after steam was turned off.

Solution heated to 105° C and steam turned off. (A sample of this de-etherized raffinate was taken for acid recovery experiment -- details under section III-O.) The remainder was neutralized to a pH of 7.15 with 20% NaOH. The solution was then heated for ten minutes (final volume 6.5 liters) and filtration tests were run (see Engineering B). There was 12 grams of dry solids for 100 cc of filtrate.

6. De-etherization and Boildown of Good Liquor

(Details under III-P - Preparation of Shotgun Sample).

J. Digestion 223 (Made by Yale group)

(2 hours - 2 X HNO_3 + 20% $NaNO_3$)

Purpose: The purpose of this run was to obtain sufficient feed solution to divide into the following portions to experiment on Mo distribution by neutralization of feed in accord with results at Princeton:

a. Un-neutralized feed saturated with $NaNO_3$ - no acid in ether (control run)
b. Feed neutralized with Na_2CO_3 to 0.10N or less
    1. use no HNO_3 in ether.
    2. use 0.10N HNO_3 in ether
    3. use 1.0N HNO_3 in ether
c. Feed neutralized with CaO to 0.05N or less
    1. use no HNO_3 in ether
    2. use 0.10N HNO_3 in ether
    3. use 1.0N HNO_3 in ether
d. Try same feed in both packed and plate tower to get quantitative comparison.

1. Digestion of Ore

132 pounds (dry basis) of ore slurry (1000 pounds uniform batch) was mixed with 26.4 pounds (20%) $NaNO_3$. The slurry was heated with stirring to 56° C and 4.5 gallons of 36° Be HNO_3 was added over a 20 minute period. Reaction was similar to 221 digestion.

After two hours' digestion, the slurry was filtered through table-top Buchners. (Largest portion of slurry cold when filtered.) Hot filtration rate was 4.78 gph/ft² with a 3/4 inch cake. Hot wash rate by displacement was 1.6 gph/ft². Total weight of dry gangue was 35.3 pounds. Volume of gangue was 1.5 ft³ wet.

2. Precipitation of Lead

Volume of DF was 60 gallons, to which was added slowly (30 minutes) in the cold with efficient stirring, 1.32 gallons of 66° Be H_2SO_4. At first the $PbSO_4$ settled slowly, but at the end of the half hour when all the acid was added, it settled quite rapidly. Good filtration rates were obtained and no trouble obtaining clear filtrate.

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Excess H_2SO_4	5.6 X stoichiometric
LC (wet)	15.9 pounds (31.7% H_2O)

3. <u>Precipitation of Excess H₂SO₄</u>

The lead filtrate was boiled down to 35 gallons and 32 pounds of BaCO$_3$ (15.3% excess) was added during one hour at 90-95° C. The slurry was digested two more hours and gave a rapid settling precipitate but it was difficult to obtain a clear filtrate.

Final volume of BF = 40 gallons - boiled down to 31 gallons (1.04N in HNO$_3$).

BC (wet) = 52.5 pounds (25% H$_2$O)

Portions of the above thirty-one gallons of BF were treated as stated in the following extractions.

4. <u>Extractions of 223 BF</u> (boiled down)

   a.   <u>Extraction 36-E</u> (Control run)

   This extraction was run as a control in order to get a comparison to the neutralized feeds in the extractions that follow. A portion of 223BF was saturated with NaNO$_3$ and no acid was used in the ether.

   <u>Feed Analysis</u>

   (223-A-FS)

Sp.G	1.5б1
XNO$_3$	370 g/l
HNO$_3$	0.98N
NaNO$_3$	206 g/l
SiO$_2$	0.13 g/l
P$_2$O$_5$	0.043 g/l
MoO$_3$	1.325 g/l

   <u>Extraction Data:</u> (Packed Tower) (1 inch x 9 1/2 ft. - 6 mm rings)

Feed rate	65 cc/min.
Solvent rate	130 cc/min.

   A very slight emulsion was observed at the top of the tower. The raffinate was turbid.

   Efficiency of Extraction = 99%

Test	Extract Analysis	Raffinate Analysis
Sp.G.	0.904	1.263
XNO$_3$	152 g/l	5.41 g/l
HNO$_3$	0.40N	
MoO$_3$	0.068 g/l	

b-1. <u>Extraction 37-E</u> (Same tower as 36-E)

This extraction was run in accord with the results on Mo distribution as found at Princeton using a feed containing practically no free HNO_3 and a solvent containing no HNO_3.

<u>Preparation of Feed</u>

Four gallons of boiled-down BF was neutralized with Na_2CO_3. A small shakeout was made on this neutralized feed to observe qualitatively how much Mo was in the extract; a fair amount was found. 180 grams more Na_2CO_3 was added bringing the total added to 980 grams - a shakeout on this indicated no detectable Mo in the extract, so the feed was filtered in preparation for running in the tower. There was only a slight turbidity in the unfiltered liquor.

On standing overnight, the clear filtrate had become turbid, but it was used without refiltering.

<u>Feed Analysis:</u> Solvent was pure ether, no HNO_3.

(223-B-FS)

Sp.G.	1.561
XNO_3	352 g/l
HNO_3	0.096N
MoO_3	1.29 g MoO_3/l
SiO_2	0.122 g/l
P_2O_5	0.043 g/l
$NaNO_3$	299 g/l

<u>Extraction Data:</u> (Same tower as 36-E)

Feed rate	20 cc/min.)	Higher rates gave emulsions
Solvent rate	40 cc/min.)	and flooding. There were emulsions at these rates but not enough to prevent operation.

Considerable precipitation formed in the raffinate in the tower. Semi-quantitative analysis by R. Mundy (Princeton) indicated approximately equal amounts of Mo and X (approximately 0.05%) and large quantities of PO_4.

Extraction Efficiency $\cong$ 99.5%

	Extract Analysis	Raffinate Analysis
Sp.G.	0.841	1.263
XNO_3	120 g/l	3.43 g/l
HNO_3	0.03	
MoO_3	0.0006 g/l	

b-2. Extraction 38-E

Same as 37-E except 0.10N HNO_3 was used in the ether in an attempt to prevent precipitation in the raffinate.

Extraction Data: (Same tower as 36-E)

Feed rate   15 cc/min.) Considerable emulsion formed
Solvent rate   30 cc/min.) at these rates but still able
                            to operate and obtain samples.

The precipitate in the raffinate was reduced to some extent using 0.10N HNO_3 in the solvent.

Extraction Efficiency ≈ 98.8%

	Extract Analysis	Raffinate Analysis
Sp. G.	0.899	1.282
XNO_3	166 g/l	3.43 g/l
HNO_3	0.076	
MoO_3	0.021 g/l	

b-3. Extraction 39-E

Same as 37-E except the use of 1.0N HNO_3 in solvent which indicated less emulsion (2/3 less) than neutral ether when both were tested in Yale's bubbler emulsion tester.

Extraction Data (Same tower as 36-E)

Feed rate   30 cc/min.
Solvent rate   60 cc/min.

There was a slight emulsion, but rates were higher than those using less acid in solvent. The raffinate also had less precipitate than in 37-E and 38-E; however, it was still quite turbid.

Efficiency of Extraction ≈ 99.3%

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	Extract Analysis	Raffinate Analysis
Sp. G.	0.902	1.282
XNO_3	143 g/1	2.54 g/1
HNO_3	0.57N	
MoO_3	0.07 g/1	

c-1. Extraction 40-E

This extraction was made on 223 BF neutralized with CaO to observe effect on Mo distribution and extraction characteristics as compared to 223-BF neutralized with Na_2CO_3.

Preparation of Feed

Four gallons of boiled down 223-BF was neutralized with 480 grams of CaO (5.8 Kg. wet $Ca(NO_3)_2$ made by H. Yeager was added). No precipitate formed, just a slight turbidity which filtered clear. A small shakeout using neutral ether was made before filtering and a slight amount of Mo was found in the extract (slightly more than when Na_2CO_3 was used.)

Extraction Data: (Same tower as 36-E) -No HNO_3 in ether.

Feed rate	30 cc/min.
Solvent rate	60 cc/min.

A bad emulsion formed and there was considerably more precipitate in the raffinate than in 37-E.

Extraction Efficiency= 99.5% (Assuming no volume change in feed to raffinate).

(223-CFS)	Feed Analysis	Extract Analysis	Raffinate Analysis
Sp.G.	1.558	0.837	1.303
XNO_3	323 g/1	106 g/1	1.75 g/1
HNO_3	<0.02N	<0.006N	
MoO_3	1.2 g/1	0.001 g/1	
SiO_2	0.424 g/1		
P_2O_5	0.042 g/1		
$Ca(NO_3)_2$	336 g/1		
$NaNO_3$	225 g/1		

c-2. <u>Extraction 41-E</u>

This is the same as 40-E except for using o.1N HNO$_3$ in the ether.

<u>Extraction Data:</u>

Feed rate	20 cc/min.
Solvent rate	40 cc/min.

The raffinate was still very turbid with a yellowish precipitate and still considerable emulsion trouble.

Extraction Efficiency = 99.7%

	Extract Analysis	Raffinate Analysis
Sp. G.	0.832	1.273
XNO$_3$	106 g/l	1.55 g/l
HNO$_3$	0.04N	
MoO$_3$	0.019 g/l	

c-3. <u>Extraction 42-E</u>

This is the same as 40-E except for using 1N HNO$_3$ in the ether in an attempt to alleviate the emulsion problem and to inhibit precipitation in the raffinate, also to observe the effect of strong acid-ether on Mo distribution when using a neutralized feed.

<u>Extraction Data:</u>

Feed rate	50 cc/min.
Solvent rate	100 cc/min.

The emulsion was considerably less than in 40-E and 41-E; also there appeared to be less precipitate in the raffinate although it was still quite turbid.

Extraction Efficiency = 99.8%

	Extract Analysis	Raffinate Analysis
Sp.G.	0.890	1.310
XNO$_3$	125 g/l	5.33 g/l
HNO$_3$	0.57N	
MoO$_3$	0.27 g/l	

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d.   Comparison of Sieve-Plate and Packed Tower

The purpose of these two runs is to compare the H.E.T.P. of the plate and packed tower. It is known by observation that a solution which emulsifies in the plate tower will not emulsify in the packed tower, which is a point in favor of packed towers. Ease of construction and wider latitude in flow rates are two more points in favor of a packed tower. One advantage of a plate tower is absence or minimum of channeling in larger diameters.

Description of Towers:

Plate Tower

Constructed of twenty-seven 1 inch x 6 inch pyrex pipe glass sections separated by stainless steel plates with one 3/32 inch hole in the center and one 3/8 inch stainless steel tube down pipe. At the top and bottom of the tower there are 1 inch to 3 inch reducing sections for separation of phases.

Packed Tower

Constructed of 19-1 inch x 6 inch pyrex pipe glass sections as above and packed with 6 mm x 6 mm glass Raschig rings. It has reducing sections at top and bottom the same as the plate tower.

e-1. Extraction 43-E   (Sieve plate tower)

The purpose of this run was to get quantitative date to compare the sieve plate extractor to the packed extractor using same feed and solvent for each extractor while using optimum operating conditions for each.

Extraction Data: $\left(\dfrac{N}{I} HNO_3 \text{ in ether}\right)$

          Feed rate   70 cc/min.
          Solvent rate   140 cc/min.

The tower operated very well. No emulsions were observed and the raffinate was free of precipitation.

Extraction Efficiency $\doteq$ 99.95% (volume changes taken
                                        into account)

880   047

Analyses

(223-D-FS)	Feed	Extract	Raffinate
Sp.G.	1.58	0.956	1.30
XNO_3	396 g/1	182 g/1	0.24 g/1
$NaNO_3$	272 g/1	.	
MoO_3	0.99 g/1	0.162 g/1	0.610 g/1
SiO_2	0.044 g/1		
P_2O_5	0.102 g/1		
HNO_3	0.40N	0.82N	0.76N

e-2. Extraction 44-E (packed tower)

The purpose of this extraction is stated under 43-E.
Same feed solution and same solvent used.

Extraction Data: $(\frac{N}{1}$ HNO_3 in ether$)$

Feed rate   105 cc/min.
Solvent rate   200 cc/min.

Some emulsion built up at these rates but was not serious.
Operating at decreased rates 70 cc/min. and 140 cc/min.
caused no emulsion.

Extraction Efficiency = 99.82% (volume changes taken
into account)

Analyses

	Extract	Raffinate
Sp.G.	0.980	1.302
XNO_3	205 g/1	0.81 g/1
MoO_3	0.062 g/1	0.666 g/1
HNO_3	0.83N	0.81N

K. Molybdenum Experiments

1. Washing and Stripping

The details of several attempts to remove Mo from the ether
extract by washing and stripping are included in the report,
Washing and Stripping Experiments to Remove Molybdenum by
H. L. Wibbels, dated 4-21-45.

The washer was made of 32 mm glass tubing; distance from
inlet to overflow was 30 inches; the top jet was 5 inches
below the overflow and had a rate of 9 c c/min. (18 feet,
head); the second jet was 13 1/2 inches below the overflow

and had a rate of 13 cc/min; the interface was kept below the inlet by continuously draining the wash water layer; a bubble separator was placed in series with the inlet to prevent undue agitation in the washer.

Following is a typical washing experiment:

Extract rate	150 cc/min. (24 EE)
Total wash rate	22 cc/min
Ratio	$\frac{H_2O}{Et_2O} = \frac{1}{6.8}$

Velocity of extract through tower (measured)   23 cm/min.

	Extract Analysis	Washed Extract Analysis	Wash Water Layer
Sp.G.	0.932		
XNO_3	146 g/l		192.9 g/l
HNO_3	0.90N		1.67N
MoO_3	0.144 g/l	0.152 g/l	0.01 g/l

Since the Mo complex seemed to give such a favorable distribution to ether, we thought it would remain in the stripped ether giving a good liquor with very little Mo. A jet stripper was designed to try this in a continuous process.

The stripper was made of 38 mm glass tubing; distance from inlet to overflow was 24 inches; the top jet was 7 inches below the overflow and had a capacity of 62 cc/min. (18 foot head); the second jet was 14 inches below the overflow and had a rate of 90 cc/min; the interface was kept below the inlet by continuously draining good liquor; a bubble separator was used as in the washer.

Following is a typical continuous washing and stripping experiment showing the distribution of Mo after leaving the extractor:

Extract rate	150 cc/min.
Wash rate	24 cc/min.
Stripping rate	152 cc/min.
Wash ratio	$\frac{H_2O}{Et_2O} = \frac{1}{10.4}$
Stripping ratio	$\frac{H_2O}{Et_2O} = \frac{1}{1.65}$

Analyses

	Extract (26-E)	Wash Water	Good Liquor	Stripped Ether
Sp.G.	1.005	1.268	1.174	0.715
XNO_3	234 g/l	276.6 g/l	192.7 g/l	0.01 g/l
HNO_3	0.96N	1.65N	0.75N	0.000
MoO_3	0.16 g/l	0.071 g/l	0.105 g/l	0.0000 g/l

As the results plainly illustrate, Mo complexes cannot be washed out of the extract or left in the stripped ether under normal washing and stripping conditions.

2.   Effect of Acidity on Mo Distribution*

The washed extracts from all of our continuous washing experiments turned green immediately after washing and turned yellow again on standing a short time. One of these washed extracts was stripped with small portions of water until practically free of XNO_3 and the ether layer was a light blue color. More water was added to complete the stripping (separatory funnel) and the blue color transferred quantitatively to the water layer. Addition of a small amount of HNO_3 transferred it back to the ether phase. This blue color was identified (by sulfide precipitation in H_2SO_4 solution) as molybdenum. It was concluded from these preliminary experiments that the distribution of Mo complexes was very sensitive to pH.

*Note: These results are also in the report Molybdenum Distribution and Preliminary Adsorpti n Study by H. L. Wibbels dated 5-2-45.

a.   Neutralization of Extract

It was thought that neutralizing the excess acid in the extract would favor the Mo complex distribution to the water layer. The plan would be to neutralize the extract and then send it through its regular wash or else attempt an alkaline wash (which would require extremely strong caustic to neutralize the excess acid using 1/10 wash ratio).

To get a complete picture widely varied HNO_3 and NaOH concentrations were used in 25 cc portions to strip 100 cc portions of unwashed extract from 26-E (0.16 g MoO_3/1). Results are in the following table.

25 cc of Stripping water	Grams MoO_3/1	
	Et_2O Layer	H_2O Layer
1.0N in HNO_3	0.14	0.0033
0.5N in HNO_3	0.136	0.0029
Pure water	0.14	0.0029
0.1N in NaOH	0.136	0.0027
1.0N in NaOH	0.136*	0.0027
4.0N in NaOH	0.110*	0.0128

*Note: Precipitate formed in these samples on standing-- probably soda salt.

As evidenced by the foregoing table, neutralization did not have much effect until the X was practically converted to soda salt.

b. Acid Stripping of Extract

From the foregoing experiment there was a slight indication that a fairly acid stripping water could be used to keep the Mo in the stripped ether.

The experiment consisted of taking 170 cc of 24-E unwashed extract and stripping successively with ten 20 cc portions of 2N HNO_3.

After the tenth portion, there was still XNO_3 in the ether layer. The stripped ether after the tenth stripping analyzed 0.16 gm. MoO_3/l. Higher value than original probably due to ether evaporation.

This method indicates possibilities but would seem impractical from the amount of nitric acid required per day. Also HNO_3 tends to salt XNO_3 into the ether layer, thus requiring more stripping water, giving a more dilute good liquor.

3. Adsorption by Charcoal.

a. Removal of Mo Complex by Charcoal

The Mo heteropolyacids being similar to organic acids, it was thought they would be adsorbed to some extent on charcoal.

13.5 grams of Merck activated USP charcoal (powdered) was mixed with 250 cc of 26-E extract (0.142 g. MoO_3/l). It was mixed and filtered immediately. The filtered extract contained 0.000 g. MoO_3/l.

Several grades of charcoal samples were ordered in an effort to determine if this adsorption was selective only to a certain type of charcoal. Results of charcoals tried to date are listed in the following table.

(Mixing with immediate filtration)

Sample Identification	Grams of Charcoal used	Extract Identification and Volume	Grams MoO$_3$/1 Before Charcoal	After Charcoal
1. Columbia Activated Carbon - Grade L 20-48 Mesh	4 grams	100 cc - 26EE	0.142	0.100
2. Columbia Activated Carbon - Grade 5P 200 Mesh	4 grams	100 cc - 26EE	0.142	0.0014
3. Same as (1) except ground to approximately 150-200 Mesh	4 grams	100 cc -26EE	0.142	0.0046

From the foregoing experiment it seems reasonable to conclude that the adsorption depends mostly on mesh size of the carbon.

Since 200 mesh charcoal would have to be used, an experiment was made to determine if a tower of this charcoal could be used through which the extract could be passed.

A tower was made of three 6 inch x 1 inch pyrex glass pipe sections only two of which were filled with charcoal which was retained by means of a plug of glass wool and Raschig rings at the inlet end and by a glass wool plug and perforated stainless steel plate at the outlet end.

A small Eastern centrifugal pump was used for pumping the extract.

The tower was filled by taking equal volumes of Nuchar T (powdered) and Columbia Activated Carbon Grade L (20-48 mesh), slurrying it with ether and pouring into the tower giving a column 1 inch x 10 inches.

Ether extract was forced through this column for about 4 inches (10 minutes) under a head of 13 psi gage. The experiment was then abandoned due to slowness of rate.

Some experiments were run by the Yale group to determine minimum amounts of charcoal required for various extracts.

The following results are from using 250 cc of extract in each experiment with the specified amount of Merck USP activated charcoal (powdered):

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Charcoal grams (for 250 cc Extract)	Extract Identification and grams MoO$_3$/l after charcoal			
	26EE	31EE	32EE	33EE
0.1	0.074	0.0035	0.141	--
0.5	0.048	0.0025	0.117	0.0003
1.0	0.018	0.0021	0.023	0.00015
4.0	0.0005	--	--	0
5.0	--	0	0.001	--
7.0	0	--	--	--
10.0	0	0	0.0003	--

Extract Analysis Before Charcoal Treatment

	26EE	31EE	32EE	33EE
Sp.G.	1.005	1.007	1.001	0.880
XNO$_3$	234 g/l	242.3 g/l	218.7 g/l	119.7 g/l
HNO$_3$	0.96N	0.80N	1.03N	0.79N
MoO$_3$	0.150 g/l	0.052 g/l	0.184 g/l	0.0014 g/l

It appears that the minimum amount of charcoal to remove the Mo from an extract like 26EE is about 0.134 lbs/gal.

b. Rejuvenation of Charcoal

If charcoal is to be used in the plant, it would be very desirable to recover the charcoal both from a cost of materials standpoint and from the cost of handling large quantities of charcoal. Hence, a series of experiments were made to see if the X and Mo could be stripped from the charcoal so that the charcoal could be used again.

It was thought that the removal of X from the charcoal could be accomplished by washing with ether and that the Mo complex could be broken with some base such as NH$_4$OH and then washed out of the charcoal. It was believed impractical to try to remove the Mo before the X was removed because the X precipitate made by introducing a basic solution into the charcoal would probably inhibit the removal of Mo.

Two 50-ml portions of 32EE (See Extraction of 220-B) were each shaken with 1 gram of charcoal (Merck USP XII).

The two portions were then centrifuged and the clear ether solutions obtained were diluted to 50 ml and analyzed for Mo and XNO$_3$. Each of the two charcoal residues were set aside to be rejuvenated.

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Each portion of charcoal containing Mo and XNO_3 were washed with three 25-ml portions of pure ether. In each wash the charcoal was separated from wash liquor by centrifugation. In each wash the ether solution was analyzed for Mo and XNO_3. The charcoal was saved to be washed with an NH_4OH solution.

One portion of charcoal received two 25-ml washes with 6N NH_4OH. The other portion of charcoal received two 25-ml washes with 12N NH_4OH. In all cases the wash liquor was separated from the charcoal by centrifugation. The washes were analyzed for Mo.

Another experiment similar to the above was tried. The only difference was the use of N ether for washing out the XNO_3.

One of the portions of charcoal which had been washed with ether and then washed with NH_4OH was then re-shaken with 50 ml. of 32EE to see if the charcoal would still remove Mo from the ether extract.

Another portion of washed and rejuvenated charcoal was ignited at 300° C and the ash was digested in H_2SO_4 and HNO_3 to determine the XNO_3 and Mo left in the ash.

Results:

Analysis of 32EE

XNO_3	0.2187 gms/ml
MoO_3	0.184 gms/l

Analyses of 32EE after Charcoal Treatment

XNO_3	0.1811 gms/ml
MoO_3	0.0013 gms/l

Analyses of Pure Ether Washes (25 ml each)

Wash No.	Gms XNO_3/ml	Gms MoO_3/l
1	0.0456	0
2	0.01022	0
3	0.00324	0

Analyses of 1N Ether Washes (25 ml each)

Wash No.	Gms XNO_3/ml	Gms MoO_3/l
1	0.0526	0.0016
2	0.01162	0.0008
3	0.00434	0.0008

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Analyses of NH$_4$OH Washes After Pure Ether Washes

Wash No.	6N NH$_4$OH Total Gms MoO$_3$	12N NH$_4$OH Total Gms MoO$_3$
1	0.006900	0.007300
2	0.000880	0.000790
Total gms MoO$_3$ Removed	0.007780	0.008090
Total gms MoO$_3$ in Charcoals before Treatment	0.0092	0.0092
Percent Removed	83.5%	88%

Analyses of NH$_4$OH Washes after 1N Ether Washes

Wash No.	6N NH$_4$OH Total Gms MoO$_3$	12N NH$_4$OH Total Gms MoO$_3$
1	0.0074	0.008450
2	0.000660	0.000850
Total gms of MoO$_3$ Removed	0.008060	0.008450
Total gms of MoO$_3$ in Charcoal Before Rejuvenation.	0.0092	0.0092
Percent Removed	87.6%	91.9%

Analysis of 32EE shaken with 1 gm of Rejuvenated Charcoal

Total amount MoO$_3$ left in extract was 56 γ. It originally contained 9200 γ. total MoO$_3$; therefore a reduction of 99.4% is represented.

Analysis of Ash from Rejuvenated Charcoal

Total grams of MoO$_3$ - 0.0011 g (or 12% of original)

It was desirable to know how often the charcoal could be rejuvenated. This experiment is not too indicative but is the only one performed to date.

Four grams of Merck USP activated charcoal (powdered) was mixed with 100 cc of 26EE (0.160 grams MoO$_3$/l) extract and filtered immediately. The charcoal filter cake was then reslurried with hot water, filtered and washed with copious amounts of hot water. The moist charcoal cake was then well mixed with 100 cc of hot N NaOH, filtered and washed with copious amounts of
I

hot water. The moist neutral charcoal cake was then well mixed with a fresh 100 cc portion of 26EE.

This four gram portion of charcoal (with rejuvenation after each use) was used to treat 9-100 cc portions of 26EE. The dried weight of the charcoal after the last rejuvenation was 3.29 grams.

The first extract after treating with the fresh charcoal had 0.001 grams $MoO_3/1$.

After the fifth 100 cc portion of extract had been treated with the 4X rejuvenated charcoal, the extract contained 0.0014 g. $MoO_3/1$.

After the ninth 100 cc portion of extract had been treated with the 8X rejuvenated charcoal, the extract contained 0.010 grams $MoO_3/1$.

As indicated under IV-K-3a, the minimum amount of Merck Charcoal to adsorb all the Mo was approximately 4 grams per 250 cc or 1.6 grams per 100 cc 26EE. There was then enough adsorbing power in this 4 grams to adsorb the maximum Mo from 250 cc of extract. This charcoal was still adsorbing at maximum after 500 cc, but after 900 cc it was only adsorbing 1/10 of the amount fresh charcoal adsorbs.

Another rejuvenation experiment was performed by the Yale group, the purpose being to try hot NaOH to see if it removes Mo better than cold NH_4OH. The experiment consisted of treating each of four 50-ml portions of 32EE (0.184 g. $MoO_3/1$) with 1 gram of Merck USP activated charcoal (powdered). The portions were well mixed and filtered. The charcoal residues were then well washed 3X with ether to remove XNO_3.

The first two portions of charcoal were then washed with two 25 ml portions of 6N NaOH (room temperature) and the other two with two 25-ml portions of 6N NaOH at 90-100° C. The charcoals were then washed with two 25 cc portions of cold water to remove the NaOH and soluble Mo.

Results of Wash with Cold 6N NaOH

Wash	Micro- Total gms MoO_3 in Filtrate
1st 25 cc NaOH	7250)
2nd 25 cc NaOH	760) total = 8010 micrograms

Results of Water Wash after 6N NaOH

Wash	Total micrograms MoO_3 in Filtrate
1st H_2O	430 micrograms)
2nd H_2O	85 micrograms) total = 515 micrograms

The total MoO_3 removed by the cold 6N NaOH and subsequent water wash was 8525 micrograms. The total micrograms in the 50 ml of extract was 9200γ, which can be assumed to be adsorbed practically 100% into the 1 gm of charcoal. Therefore, the charcoal still retains 7.3% of the Mo.

Results of Wash with Hot 6N NaOH

Wash	Total micrograms MoO_3 in Filtrate
1st 25 cc NaOH	7350)
2nd 25 cc NaOH	840) total = 8190 micrograms

Water Wash After Hot 6N NaOH

Wash	Total micrograms MoO_3 in Filtrate
1st H_2O	460)
2nd H_2O	80) total = 540 micrograms

The total MoO_3 removed by hot 6N NaOH and water washes was 8730 micrograms. This represents 5% of the Mo still in the charcoal.

4. Other Adsorbents Than Charcoal

Since removal of Mo complexes from the extract by charcoal seemed to be a pure adsorption, it was thought other common adsorbents might work.

a. Silica Gel

100 cc of 26E Extract (0.16 g. MoO_3/l) was mixed well with 10 grams of Silica Gel (labeled 6595-8-2000-Davidson Chemical Co.) and filtered immediately. Analysis of the filtrate indicated 0.126 g. MoO_3/l or 21.2% Mo removal.

This silica gel was about the mesh of fine sand. It was obtained from Dr. Harrington of M.C.W. It did not lose its identity in the acid-ether extract or when standing around several days in water.

880   057

b.   Charcoal Ash (constitutes approximately 4% of the charcoal)
     (28% Mo removed)

It was thought by Dr. Harned of Yale that the ash of the char-
coal might be adsorbing or breaking up the Mo complexes. A
portion of Merck Activated Charcoal was ignited and 2 grams
of the ash was used to treat 50 ml of 32E extract (0.222 g.
MoO_3/l). On standing 48 hours, the treated extract contained
0.150 g. MoO_3/l or 28% Mo removal.

c.   Activated Alumina (18.5% of Mo removed)

50 ml of 32E extract (0.222 g. MoO_3/l) was treated with 2
grams of Activated Alumina. On standing 48 hours the treated
extract contained 0.180 g. MoO_3/l or 18.5% removal of Mo.

d.   Ferric Oxide (ignited): (46% Mo removed)

Two grams of Fe_2O_3 (ignited) was used to treat 50 ml of 32E
extract (0.222 g. MoO_3/l). The treated extract on standing
48 hours contained 0.120 g. MoO_3/l.

Since powdered charcoal adsorbs 99+% of the Mo immediately, none
of these common adsorbents as used here compared favorably to
powdered charcoal.

Another method of attack was tried and that was to "tie up" the
phosphate or silicates, which form the complexes, as some insoluble
or unreactive compound and thus change the Mo to a non-ether-
soluble form and keep it in the feed and raffinate.

The only experiments along these lines tried to date are as follows:

To 25 cc of 223A feed solution was added 0.3 grams of $Fe(NO_3)_3 \cdot 9H_2O$.
This was treated to one shakeout with 50 cc of ether 1N with HNO_3.
The resulting extract contained 0.0107 g. MoO_3/l.

Another experiment same as above except using 0.60 grams $Fe(NO_3)_2 \cdot$
$9H_2O$ gave an extract containing 0.0096 grams MoO_3/l.

5.   Low Acid Digestions and Feed Neutralization

It was found that the extract from the 1.3X digestions (218 and
219) contained something on the order of 0.003 to 0.006 grams
MoO_3/l even when using 1N HNO_3 in the solvent. The feeds were
0.01 and 0.005N respectively. It is believed that in these low
acid digestions very small amounts of the ether soluble Mo com-
plexes are formed.

830   055

After our findings on the effect of acidity on the distribution of
the Mo complex between ether and water, Princeton started working
on the problem and soon found that neutralization of the feed with
Na_2CO_3 or CaO and using no acid in the ether gave an extract with
practically no Mo.

Results of Neutralization of Feed by Princeton

Feed used was 220D containing 2.20 grams MoO$_3$/l. Procedure consisted of shaking once with an equal volume of neutral ether.

As a result of the above experiments it was decided to try running some neutralized feed in the continuous tower at Yale.

Princeton's Results Table

| Trial	gms Na$_2$CO$_3$ per 100 cc of Feed	Extract Gms MoO$_3$/l	N of HNO$_3$ in Feed Solutions
1*	5	0.0047	--
2	0	0.70	0.85
3	3	0.644	0.35
4	4	0.11	0.19
5	5	(ppt formed & discarded)	

* 1 is original solution; 2, 3, 4, & 5 are the original solution saturated with NaNO$_3$.

Digestion 223 was made for the sole purpose of obtaining enough uniform feed solution to try various neutralization experiments. Details of this digestion and subsequent extractions can be found under IV-J.

Following is a table with a summary of the results on neutralizing the feed. (Packed tower used.)

% Efficiency of Extraction	Feed Solution Identity	Neutralizing Agent	N of HNO$_3$ Feed	N of HNO$_3$ Solvent	gms MoO$_3$/l Feed	gms MoO$_3$/l Extract	Comments
99.	223A-36E	None		0.0	1.325	0.068	Good flow rates - very slight emulsion.
99.5	223B-37E	Na$_2$CO$_3$	0.096	0.0	1.29	0.0006	Very low rates - bad emulsions - precipitate in raffinate.
98.8	223B-38E	Na$_2$CO$_3$	0.096	0.1	1.29	0.021	Very low rates - considerable emulsion - slight precipitate in raffinate.
99.3	223B-39E	Na$_2$CO$_3$	0.096	1.0	1.29	0.07	Low rates - emulsions - turbid raffinate.
99.5	223C-40E	CaO	<0.02	0.0	1.2	0.001	Low rates - bad emulsion - lot of precipitate in raffinate.
99.7	223C-41E	CaO	0.096	0.1	1.29	0.019	Very low rates - bad emulsion - considerable precipitate in raffinate.
99.8	223C-42E	CaO	0.096	1.0	1.29	0.27	Moderately high rates - slight emulsion - turbid raffinate.
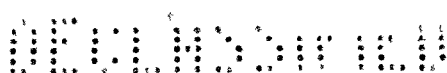
Neutralisation of the feed multiplies our emulsion problem
and it also cuts our extraction efficiency especially if
high P_2O_5 ores would be used.

L. Emulsion Experiments

1. Boildown of Feed Solutions

In experiments in both the laboratory and plant at MCW some
success had been attained in reducing the emulsion problems
in a batch extractor by boiling down the feed solutions to
a temperature higher than the boiling point of pure $XO_2(NO_3)_2$.
$6H_2O$. Hence, it was decided to try this on some of the feed
solutions which emulsified at Yale.

300 ml of 219-FS (See Extraction 29-E) was concentrated to
a boiling-point of 140° C. The solution was then diluted
to its original volume. A red precipitate was formed during
the boildown and did not go back into solution when the
liquor was diluted. The solution was then filtered. The
residue was washed with water and dried. The weight of the
residue was 0.815 grams, and a sample was sent to MCW for
identification of elements present, especially Si. The
filtrate was tested in the bubbler and no emulsion could
be formed. The acid in the ether was varied from 0 to
approximately 1N. No emulsion could be made with any of
the various acid concentrations; however, when the acid
concentration was as low as 0.15N, a yellow precipitate
formed in the water layer after most of the XNO_3 had been
extracted.

Another 300 ml portion of 219-BF was concentrated to 120° C
instead of 140° C, diluted and filtered. The extraction
test again gave no emulsion.

A 300 ml portion of 216-BF (See Extraction of 216 Liquors)
was concentrated to a boiling point of 120° C, diluted to
original volume and filtered. The extraction test on the
filtrate gave no emulsion.

A 300 ml portion of 216 MFS (See Extraction of 216 Liquors)
was concen rated to a boiling point of 150° C, diluted to
original volume, and filter·d. The extraction test gave
no emulsion.

2. Charcoal Treatment of Feed Solutions

One 300 ml portion of 216-MFS was thoroughly mixed with 1
gram of Merck Activated Charcoal (USP XII) and allowed to
stand for an hour with occasional slushing. Another 300 ml

880 CCU

portion of 216-MFS was treated in a similar manner with 5 grams of the same charcoal. Both solutions were filtered and tested in the bubbler. In both cases an emulsion was formed.

3. **Water Spray for Breaking Emulsions**

No detailed experiments were made to determine if a fine spray of water would break an emulsion. However, in at least three runs in the small bubbler in which emulsions had formed, the emulsion was easily broken by squirting a small stream of water from a wash bottle into the ether layer in the bubbler. The emulsion breaks almost instantaneously as the drops of water pass through; however, after the water has passed through, the emulsion forms again.

4. **Miscellaneous Emulsion Experiments**

Some of the 223B feed solution (neutralized with Na_2CO_3) which gave a bad emulsion in the packed tower was tried in Yale's bubbler emulsion tester. Neutral ether was used for this test. (This bubbler simulates a single section of their plate tower except the water phase is not continuously drained and feed is not continuously added.) A bad emulsion was formed immediately. The water phase was drained and the emulsion layer and clear extract were saved. After washing out the bubbler, the partially extracted water layer was put back in and ether run through it again with formation of an emulsion. The water phase was drained and the procedure was repeated three times; on the fourth trial no emulsion formed. A portion of the water layer from a similar experiment using same feed and solvent was saturated with M.C.W. Chemical 253 ($XO_2NO_3.6H_2O$) until the specific gravity exceeded that of the original feed. It was then tried in the bubbler again with no emulsion formation at all.

Samples of emulsion layer, clear extract, and extracted emulsion-free water phase were taken by R. Mundy of Princeton for analysis.

Results:

a. **Emulsion Phase**

Total Volume - 50 cc (46 cc clear extract (discarded)
(4 cc aqueous

SiO_2	Mo	P_2O_5	Fe	Insol. from SiO_2 (prob. $BaSO_4$)
0.020	0.115	0.023	0.144	0.362

b.. Raffinate Phase

Standing overnight produced a precipitation - 30 cc
of raffinate centrifuged gave 3.75 cc of precipitation.

	SiO_2	Mo	P_2O_5	Fe	Insol. from SiO_2 (prob. $BaSO_4$)
Ppt.	0.001	0.049	0.010	0.053	0.139
Clear Raffinate	0.000	0.029	0.004	0.029	0.258
Total	0.001	0.078	0.014	0.082	0.397

The greatest difference between the water phase from
the emulsion layer and the raffinate is their silica
content (20X). The water phase from the emulsion layer
is from 0 to 2 times greater in the other analyzed
constituents than the raffinate.

M. Roasting of Ore for My Distribution

600, grams of AAA ore (69% X_3O_8 - through 40 mesh) was thoroughly
mixed and divided into three portions, A, B, and C. Portion A
was roasted in the presence of air. Portion B was mixed with 5
grams of activated charcoal. Portion C was held as a control
for comparison with either of the other two.

Portions A and B were roasted in a muffle furnace at 265° C for
18 hours.

Each of the three portions were then digested in 2X HNO_3, filtered
and washed with hot water. The gangues were sampled to be analyzed
for X and My. The filtrates from A and B were sampled to be
analyzed for X and Mo. Sample C was used in a beaker experiment
for precipitation of sulfate as $CaSO_4$.

Analyses:

	My In Gangue	XNO_3 In Gangue	$\%$ X Recovery
Portion A	39×10^{-8} gms/gm	0.0400 gms/gm	99.3
Portion B	38×10^{-8} gms/gm	0.0562 gms/gm	99.1
Portion C	42×10^{-8} gms/gm	0.0506 gms/gm	99.0

	XNO_3 g/ml	MoO_3 μ/ml
Portion A Filtrate	0.282	740
Portion B Filtrate	0.308	590

N. Precipitation of Excess H_2SO_4 as $CaSO_4$

In some of the $BaSO_4$ filtrations, difficulty was encountered in
getting a clear filtrate and also the filtration rate was variable.

Because $CaSO_4$ filters easier than $BaSO_4$, it was thought that most of the excess sulfate after the Pb removal might be precipitated as $CaSO_4$ in the presence of a large quantity of $Ca(NO_3)_2$ which could be used as a salting agent. If the precipitation of sulfate as $CaSO_4$ was insufficient it was thought that a double precipitation of $CaSO_4$ and $BaSO_4$ might filter easier than a single precipitation of $BaSO_4$.

The filtrate from a 100 gm digestion used as a control digestion for roasted ore (Portion C) was used in this experiment.

Assuming 6% PbO in the ore, it was calculated that 9.4 ml of 66° Be H_2SO_4 would be required to precipitate the Pb as $PbSO_4$. This quantity was added to the solution and found to be sufficient by testing for completeness of precipitation. The $PbSO_4$ was removed by filtration through a Buchner funnel.

The amount of excess H_2SO_4 in the solution was calculated to be 14.5 grams. 10.95 grams of $Ca(OH)_2$ was added to the solution to neutralize the excess H_2SO_4. 57.8 grams of $Ca(NO_3)_2 \cdot 4H_2O$ was then added to the solution to approximate a feed solution containing 300 grams per liter of $Ca(NO_3)_2 \cdot 4H_2O$. Upon the addition of $Ca(OH)_2$ only a slight amount of precipitate formed. However, there was considerable precipitation when the $Ca(NO_3)_2$ was added. The solution after the addition of $Ca(NO_3)_2$ was 800 ml. The solution was concentrated to 200 ml, at which time the solution was cooled. Upon cooling there was considerable crystallization. The solution was diluted with water to about 300 cc to dissolve the $Ca(NO_3)_2$ crystals and filtered. The $CaSO_4$ cake was washed with 100 cc of H_2O. The weight of the dried cake was 8.2 grams, which is equivalent to 5.9 grams of H_2SO_4. Therefore, the percent of the sulfate precipitated was 40.2%.

The $CaSO_4$ and the filtrate were then slurried again and heated to boiling. The stoichemetric amount of $BaCO_3$ required to precipitate the remaining 59.8% excess sulfate was added to the boiling solution and digested for fifteen minutes at the boiling temperature. The hot solution was then filtered through an 11 cm Buchner funnel using No. 1 Whatman paper. The filtration was rapid and a clear filtrate was obtained immediately.

O. Acid Recovery From Raffinate

The purpose of this experiment was to see if nitric acid could be recovered to any extent from the raffinate.

250 cc of 222-35E-R (Raffinate from 2.5 X - no $NaNO_3$ digestion) was taken after de-etherization (during which some brown fumes were lost). It was 1.65N in acid.

The apparatus used for distillation consisted of a 500 cc distilling flask with a thermometer placed in the liquor, a bulb condenser, and an adapter, the end of which was kept beneath the distillate throughout the distillation to prevent undue losses of HNO_3.

Flame was removed after boiling had started at 105° C. No auto reaction was observed, so distillation was continued. Moderate brown fumes came over at first. They did not dissolve in the distillate and so were lost. The distillation was continued until the temperature reached 148-150° C. The volume of distilland was estimated at 30 cc. It was yellow and viscous and started to crystallize on cooling.

The volume of distillate and wash from the condenser was 250 cc, 1 cc of which was equivalent to 12 cc of 0.105 N NaOH or 1.26 N representing a recovery of

$$\frac{1.26}{1.65} \times 100 = 76.5\%$$

The still residue was diluted to 250 cc with water. The precipitate coagulated when boiled, leaving a clear, colorless, supernatant water layer. The above cooled slurry was neutralized (alkaline to litmus) with 80 cc of approximately 20% NaOH solution. It filtered only at a moderate rate, giving a very gelatinous cake.

P.   Preparation of Shotgun Sample

Most of the chemical and spectrographic analyses of the good liquor made at Yale indicated that the material made by adsorbing the Mo in charcoal and washing the other impurities from the ether extract would pass practically all of the chemical specifications for Chemical 306. However, it seemed advisable to prepare enough good liquor for a shotgun analysis, and it was decided to prepare some good liquor from the ether extract from Digestions 221 and 222.

1.   Good Liquor From Digestion 221

6.2 gallons of ether extract from Digestion 221 (221-34-EE) was treated with 2.17 pounds of Merck Activated Charcoal (USP XII). The slurry was stirred in a 20-gallon tank. The slurry was then filtered through a single frame stainless steel press made by clamping one frame between two plates using C-clamps. The filter media was glass cloth, which was precoated with about 1/8 inches of filter cell. The filtration was rapid and clear.

580   064

The ether extract was then washed in the spray washer at a washing ratio of 1/11.9 (water:ether extract) and stripped in the spray stripper at a stripping ratio of 1/1.7 (water:ether). (For analyses of the products from these operations see "G. Digestion 221". The volume of water extract obtained was 3.96 gallons.

The water extract was transferred to a five gallon stainless steel tank to be de-etherized. The solution was de-etherized in 12 1/2 minutes, using a steam coil. The temperature range was 19° C - 102° C. No trouble was encountered and there were no brown fumes.

2. Good Liquor From Digestion 222

4.78 gallons of ether extract from Digestion 222 (222-35-EE) was treated with 1.6 pounds of Merck Activated Charcoal (USP XII) in the same manner that the extract from Digestion 221 was treated. The filtration through the single frame press was again rapid and clear.

The ether extract was washed and stripped using the same washing and stripping ratios as had been used for 34-EE. (For analysis of products in these operations, see "H Digestion 222").

The water extract was then de-etherized to a temperature of 80-90° C in a 5 gallon stainless steel tank. At this temperature, the de-etherized good liquor from Digestion 221 was poured in with the solution being de-etherized. When the temperature of combined solutions reached a temperature of 95° C, a vigorous reaction started with the evolution of brown fumes. This reaction continued with the steam off for about ten minutes. It was thought that the high acid concentration in the extract from Digestion 222 was the cause of the reaction.

The mixture of the two solutions was then concentrated in the five gallon tank and crystallized. After about two hours of concentration, it was discovered that the stainless steel lid on the tank had two brass rivets in it. Hence, the good liquor was probably contaminated.

By an ignition to X_3O_8 assay of the solution, the amount of X in the form of good liquor was calculated to be 6.6 pounds. This good liquor was combined with 15.6 pounds X as XO_2, which had a shotgun of 0.02 ± 0.05% (without assay). A shotgun analysis was made of this mixture equivalent to 22.2 pounds X.

Results:

MCW Sample #70	0.04 ± 0.05%
Total	0.04
Contributed by 15.6 pounds is $\frac{15.6 \times 0.02}{22.2}$ =	0.014
Contributed by 6.6 pounds =	0.026

$0.026 \times \frac{22.2}{6.6}$ = 0.0875 shotgun result on our 6.6 pounds of metal.

Q. Test for Precious Metals

Since the filtrate from the caustic precipitated raffinate (also sump liquors in plant) is the only portion of material in this process likely to go down the sewer, it was advisable to have some of this liquor tested for precious metals.

A portion of the filtrate from the precipitated raffinates from extraction 43 and 44 was boiled down until upon cooling a solid crystal mass was formed. Spectrographic analysis of this crystalline material at M.C.W. gave the following results:

	43	44		43	44
Ag	N	N	Mn	N	N
Al	L-S	L-S	Mo	L-S	L-S
As	N	N	Na	C	C
Au	L	L	Ni	N	N
B	L	L	Os	N	N
Ba	L	L	P	N	N
Be	N	N	Pb	N	N
Bi	N	N	Pd	L	L
C			Pt	N	N
Ca	L-S	L-S	Rb	N	N
Cb	N	N	Re	N	N
Cd	N	N	Rh		
Ce	N	N	Ru		
Co	N	N	Sb	N	N
Cr	N	N	Sc	N	N
Cs	N	N	Si	L	L
Cu	L	L	Sn	N	N
F	N	N	Sr	L-S	L-S
Fe	L	L	Ta	N	N
Ga			Th		
Ge	N	N	Ti	N	N
Hf			Tl	N	N
Hg	N	N	U	N	N
In	L	L	V	N	N
Ir	N	N	W	N	N
K	N	N	Y		
La	N	N	Zn	N	N
Li	N	N	Zr	N	N
Ma			Sm	N	N
Mg	L	L			