

インドネシア共和国原子力庁 核物質開発センター出張報告書

平成3年度原子力研究交流制度に基づく事業団技術者の派遣

1991年 11月

動力炉・核燃料開発事業団

人形峠事業所

複製又はこの資料の入手については、下記にお問い合わせください。

〒708-06 岡山県苫田郡上斎原村1550番地
動力炉・核燃料開発事業団
人形峠事業所
ウラン濃縮工場・技術課

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Engineering Section, Uranium Enrichment Plant, Ningyo Toge Works,
Power Reactor and Nuclear Fuel Development Corporation,
1550 Kamisaibara-son, Tomada-gun, Okayama-ken, 708-06, Japan

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(Power Reactor and Nuclear Fuel Development Corporation)

1991年 11月

天 本 一 平^{*1}
広 野 修一郎^{*2}

要 旨

平成3年度原子力研究交流制度に基づき、事業団技術者として、インドネシア共和国のインドネシア原子力庁核物質開発センターを訪問し、同センター技術者との研究交流を10月22日より11月4日まで行った。

今回の訪問目的は、インドネシアが建設した粗製錬パイロットプラントを順調に稼働させるための技術的検討を行うもので、当初、核物質開発センター側は、特にウラン製錬残液のイオン交換に関する研究交流を希望していた。しかしながら、実際に検討した内容は、ウランのヒーブリーチング工程より、イエローケーキの脱水・乾燥工程に至るウラン粗製錬に関する全範囲に及んだ。

PNCとしては、核物質開発センター側が抱える諸問題について、これまでに主として人形峠事業所が蓄積させてきた技術や経験を基に解析し、可能な限りのアドバイスを行うと共に、持参した浮選試薬を用いて、ウラン鉱石中の有価鉱物の回収試験を実施し成果を得ることができたが、今回の派遣にて核物質開発センター側の問題が全て解決されたわけではないので、引続き、同国に対する研究交流を推進していく必要があるように考えられる。

*1 転換技術開発課

*2 人形峠原子力産業(株) 総務部長

インドネシア共和国原子力庁
核物質開発センター出張報告書

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*2 人形峠原子力産業課 総務部長

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1. 派遣名称

平成3年度原子力研究交流制度に基づく事業団技術者の派遣

2. 派遣期間

1991年10月22日～11月4日

3. 相手国、対象機関及び所在地

(1) 相手国名称：インドネシア共和国

(2) 対象機関名：インドネシア原子力庁核物質開発センター (Pusat Pengembangan Bahan
Galian Nuklir: Nuclear Material Development Centre)

(3) 所在地：ジャカルタ市 Cinere Jum'at 通り (Jln. Cinere, Ps. Jum'at, Jakarta)

4. 目的

平成3年度原子力研究交流制度の一環として、インドネシア共和国原子力庁核物質開発センター（以下、センターという）に赴き、粗製錬に関する研究交流を行うことを主たる目的とする。今回は、インドネシア共和国が建設し、運転を実施している粗製錬パイロットプラントに対する技術交換を行い、同プラントが順調に稼働するように検討をする。インドネシア共和国側の希望としては、ヒープリーチング工程、イオン交換精製工程及び浮遊選鉱法に関する検討を行いたいとのことである。

5. 交通手段

成田空港より、インドネシア共和国へは、ガルーダ航空が唯一の直行便として運行している。所要時間は7時間30分である。インドネシア共和国ジャカルタ市の空の玄関であるスカルノ・ハッタ空港より、ジャカルタ市内までは、タクシー等で約1時間の距離である。

今回の出張では、ジャカルタ市の新興市街地である「ブロックM」のホテルに宿泊した。「ブロックM」よりセンターまでは、車で約30分かかる。

6. インドネシア共和国における留意点

インドネシア共和国では、少なくとも以下の点に留意すること。

(1) 共通言語は、インドネシア語であるが、ホテルや事務所では英語が通じる。

(2) 同地では、飲料可能な水道水はないので、必ず、ミネラルウォーター等を飲料水とすること。

(3) 電話事情が非常に悪いのでその点を考慮しておくこと。

- (4) 敬虔なイスラム教徒が多いので、その文化と伝統を尊重すること。

7. 研究交流実施事項

7.1 体制

製錬転換に係るインドネシア原子力庁体制図を図-1に示す。今回の派遣では、センター内の鉱石処理部(Division of Ore Processing)を訪問し同部において主として粗製錬に関する研究交流を行った。

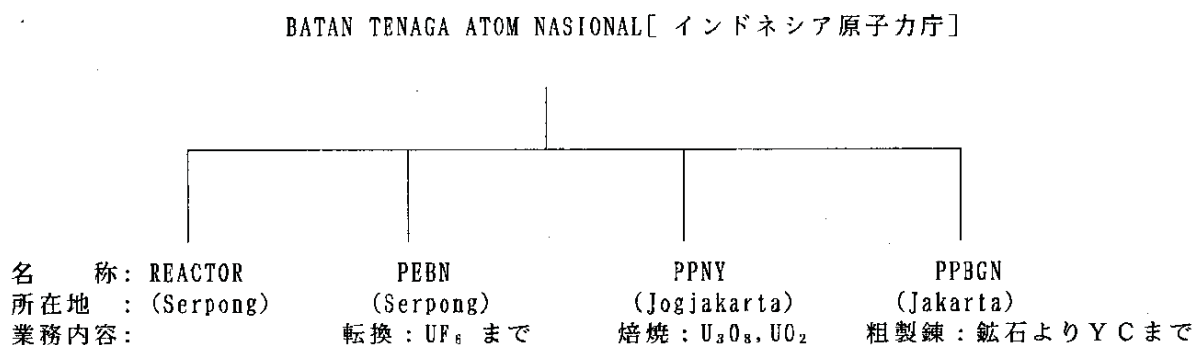
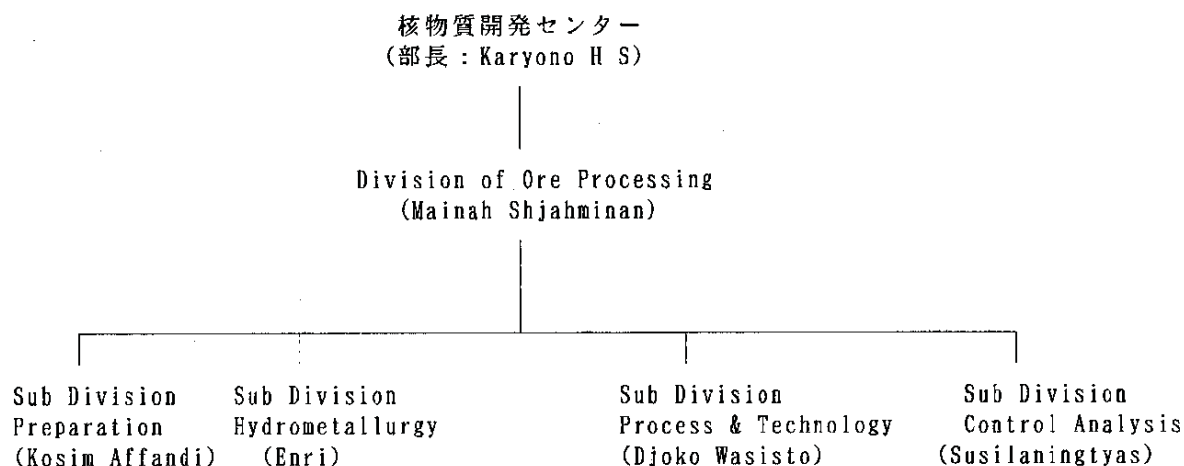


図-1 製錬転換に係るインドネシア原子力庁体制図

7.2 組織

センター側の製錬に関する組織について図-2に示す。



() 内は各課室の責任者名称

図-2 核物質開発センター側粗製錬関係組織図

7.3 粗製錬パイロットプラントの運転状態

インドネシア側粗製錬パイロットプラントの運転状態は下記のようなものである。なお、各年度毎の運転月数は、3ヶ月(12～2月)である。

表-1 粗製錬パイロットプラントの運転状態

期 間	運 転 状 態
1981 年～ 1985 年	運 転
1985 年～ 1990 年	休 止
1990 年～ 現在	運 転

7.4 研究交流内容

今回、実施した研究交流内容について以下に示す。

(1) インドネシア側粗製錬パイロットプラントの技術的問題点の検討

- ① ヒープリーチング工程について
- ② 粉碎工程について
- ③ 固液分離工程について
- ④ 精製工程について
- ⑤ 沈殿工程について

(2) 基礎試験

鉱石中の硫化鉄(FeS_2)及び硫化モリブデン(MoS)を有価鉱物として回収するための浮遊選鉱試験

(3) その他の技術的検討

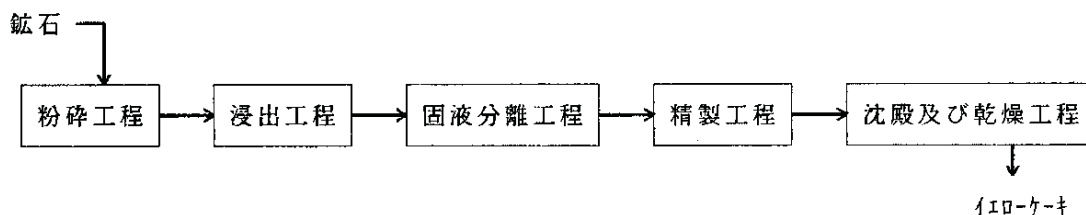
- ① liquid membrane について
- ② 分析技術について
- ③ 機器・試薬等について

7.5 研究交流詳細

7.5.1 インドネシア側粗製錬パイロットプラントの概要

(1) インドネシア側粗製錬パイロットプラントのフローシート

インドネシア側粗製錬パイロットプラントのフローシートを図－3に示す。



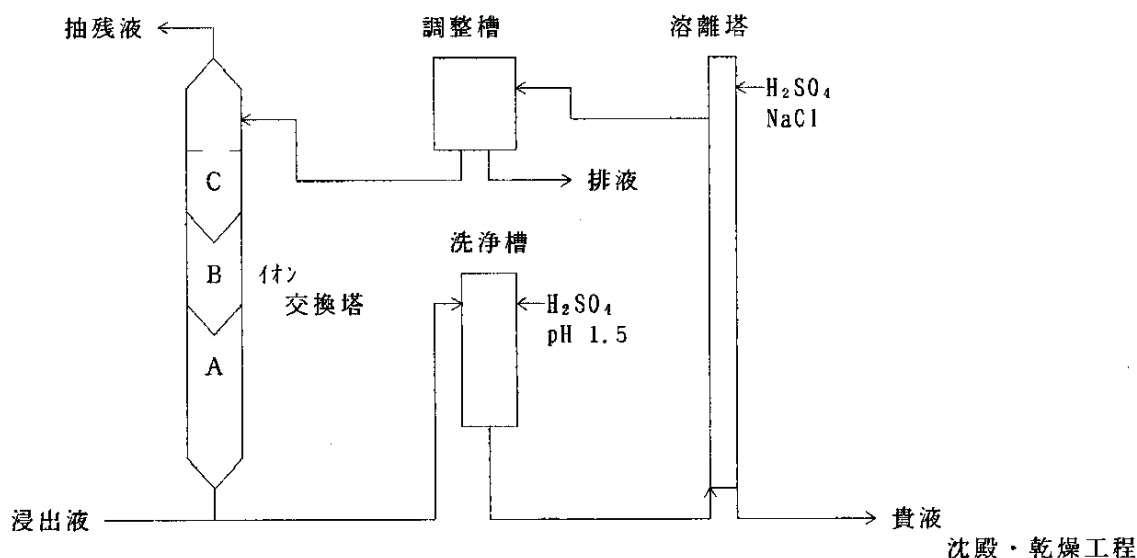
図－3 粗製錬パイロットプラントのフローシート

図－3にみられるようにインドネシア側粗製錬パイロットプラントのフローは、通常のウラン鉱山でみられるフローとほぼ同様な工程により構成されている。

即ち、採掘されたウラン鉱石は、粉碎工程にて平均－48meshの粒径に粉碎・分級される。粉碎・分級された鉱石は、浸出工程に運ばれ、硫酸溶液を用いたウラン浸出が行われる。この時の、ウラン回収率は最大70%である。浸出液は、固液分離工程に送液され、シックナーで向流デカンテーション法により固液分離され、ウラン回収率は90%である。

上澄液は精製工程に送液され、イオン交換法によりウラン精製が行われる。本パイロットプラントのイオン交換には Humsley system を採用しており、イオン交換樹脂としては、IRA-400 を用いている。

図－4に本プラントにおけるイオン交換工程概略を示す。



精製された貴液は、沈殿及び乾燥工程に送液し、同工程でアンモニア水を用いて、イエローケーキ(ADU)を製造する。イエローケーキについては横型流動乾燥機により乾燥される。

このパイロットプラントの操業条件を表-2に示す。

表-2 カリマントンパイロットプラントの操業条件等*

項 目	操 業 条 件 等
1. 鉱石処理量	150 kg/hr.
ウラン鉱物の種類	Uraninite, Brannerite
2. 浸出工程：	
鉱石粒度	60 %：-48mesh，40 %：-100mesh
設備	攪拌槽 4 基直列
パルプ濃度	50 %-solid
硫酸使用量	150kg/t-ore
酸化剤	MnO ₂ ：20kg/t-ore
時間	8 時間
温度	70℃
p H	1.5
E h	>430mV(最終段階)
3. 固液分離工程：	
設備	シックナー 4 基直列
4. イオン交換工程：	
設備	Humsly SIX
イオン交換樹脂	Amberlite IRA 400
5. イエローケーキ 沈殿工程：	
方法	アンモニアによる沈殿
6. ウラン回収率	50 %～ 60 %

* 1990 年に行った操業条件で、それ以前の操業条件（付録-1 参照）と多少異なる。

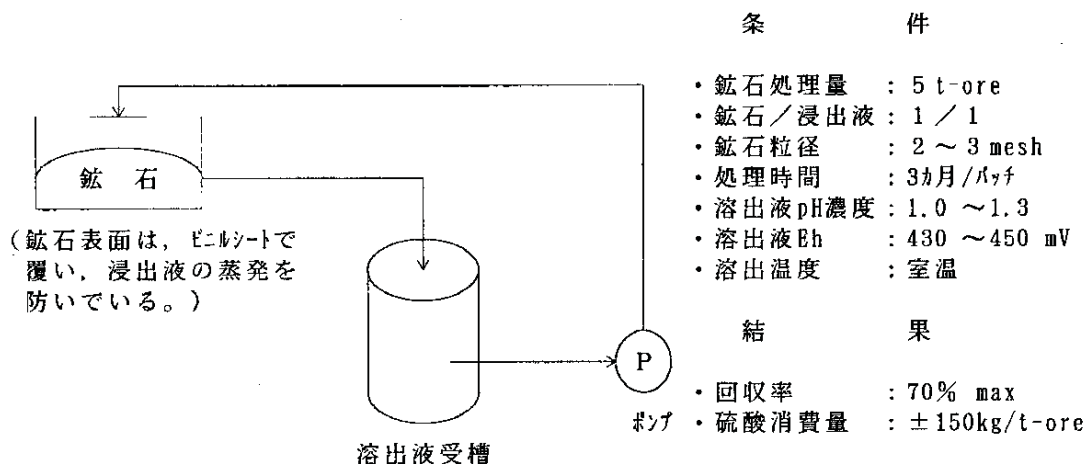
7.5.2 インドネシア側粗製錬パイロットプラントの技術的問題点の検討

(1) ヒープリーチング工程について（ヒープリーチング工程概略を図-5に示す）

①インドネシア側の問題点

(イ) 珪酸 (SiO_2) が堆積物表面やポンプに蓄積したり、また、貴液に溶出し同工程や以降の工程に悪影響を及ぼす。

(ロ) 収率が±70%と低い。



②検討結果

(イ) SiO_2 については、固液分離工程で除去することを試みる。また、硫酸濃度を SiO_2 の溶出が少なくなるような濃度に下げしてみる。さらに、浸出時間を現状の3ヶ月より短縮してみる。その結果、ウラン溶出率は低下するだろうが、低品位ウラン鉱を処理する場合には、経済性を鑑みて収率を低下させても SiO_2 が析出しないような条件を設定する。即ち、製錬へ供給する鉱石を採掘する際に、どうしても低品位鉱が伴って出鉱されるため、それをそのまま捨ててしまうよりも経済的に、かつ、簡便にウランが回収されるならば、ウラン回収率に重点を置かずにヒープリーチングを行ったほうがよい。

なお、根本的解決策ではないが、ポンプについては、閉塞しないような構造のものがあるので日本国内のメーカーに問い合わせて後日連絡する。

(ロ) 上述(イ)の事実を踏まえて、収率よりも SiO_2 が析出しないような適正 pH 条件を優先させる。

- (ハ) その他の総合的な検討結果として、本試験では、5 t-ore 規模の試験しか実施しておらず、同試験結果は、必ずしもベンチスケール試験の結果と一致しない。
- よって、少なくとも、500t-ore規模の試験を実施してみる。方法は現地（カリマンタンの採鉱場付近）の地面にプールを造り、ビニルシート等で漏水・防水加工をした後、鉱石をヒープし、浸出液をリサイクルさせて経時変化を観察することを提案した。

(2) 粉砕工程について

①インドネシア側の問題点

- (イ) 粉砕及び選鉱に関する方法、機器についての情報が十分でない。
- (ロ) 重金属を主とした不純物を有価鉱物として回収したい。

②検討結果

- (イ) 粉砕に関しては、粉砕粒度が、一般の鉱山で行われている前処理の粒度に比較して荒すぎる。よって、粉砕方法をさらに検討すべきである（付録－1 参照）。粉砕機については通常の機器にて十分であるが、詳細情報については、後日連絡する。
- (ロ) 重金属等の不純物の回収については、今回は浮選試薬を持参したので、同試薬を用いた浮選試験を実施する。

(3) 固液分離工程

①インドネシア側の問題点

- (イ) インドネシアでは固液分離を向流デカンテーション(CCD)方式により行っているが、スラリーが抜き出し部をよく閉塞させるため、同抜き出し部及びスラリー送液ポンプを改善したい。
- (ロ) シックナーの自動化を図りたい。
- (ハ) ろ過機の改造を行いたい。CCD 後のろ過剤として、現在、砂を使用しているが、砂の中の SiO_2 が溶出して、次工程である精製工程に悪影響を及ぼすので、ろ過剤の変更を図りたい。

②検討結果

- (イ) シックナーの形状及び基数に問題があるようである。即ち、閉塞防止策としてはシックナーの形状を図－6に示すように貯槽型のものより、通常のシックナー型

のものに変更した方がよい。つまり、シックナーの高さを下げて単位面積当たりにかかる圧力を低下させ、スラリーの抜き出しを容易にすることが問題解決の一手段であろう。また、シックナーの基数については、インドネシア側の4基は十分な固液分離を行っていく上で少ないので、一般的に必要とされるシックナーの基数である6～8基に増設されることを提案する。さらに、シックナー内の液の滞留時間が十分ではないように考えられるので、基礎試験により最適滞留時間を設定すればよい。即ち、次工程で SiO_2 の沈積による問題が生じているので、固液分離工程で十分に SiO_2 を沈積させる設備と滞留時間を設定することが必要である。なお、上記の詳細な設計については、基礎試験により必要なデータ（沈降速度等）を取得した後、シックナーの専門メーカーに設計させれば簡単に解決できる。スラリー送液ポンプについては、日本国内の専門メーカーと協議の上回答する。

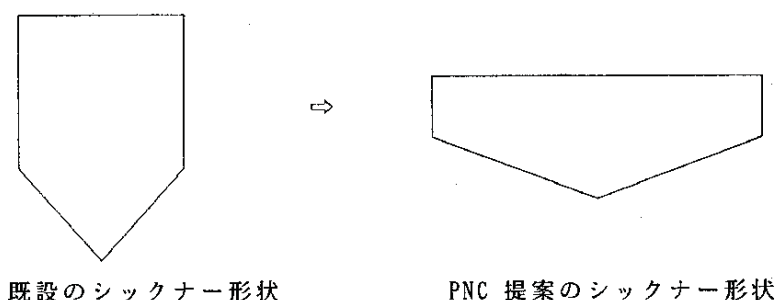


図-6 シックナーの形状の変更

(v) シックナーの自動化については、レベル計が中心となるように考えられるので、専門メーカーに問い合わせの上、詳細は回答する。

(ハ) ろ過機については、各種構造のものがあり、大差はないと考えられるが、強いて米国(Kerr-McGee 社)の使用例を挙げれば、加圧ろ過機を採用しており、商業規模で稼働中である。

ろ過剤としては一般的に使用される砂以外に鉄系のものもある。但し、鉄系のろ過剤にしても、本パイロットプラントの条件では鉄が不純物として浸出液中に溶出するために問題解決とはならない。よって、以下のことを本工程の問題を総合的に踏まえた上で提案する。

(i) 浸出液の不純物では SiO_2 が問題になっている。 SiO_2 については固液分離工程で除去することを試みる。これには基礎試験で、浸出費液からの SiO_2 固体発生量と経過時間との関係を詳しく調べることが最も重要である。

- (ii) SiO_2 は固液分離工程で水酸化カルシウム($\text{Ca}(\text{OH})_2$)を添加して、浸出液の pHを 2～2.5 に調整し、石膏(CaSO_4)と SiO_2 を共沈させることにより除去できる可能性がある。
- (iii) pH値の低い溶液をろ過するのに、砂ろ過は一般に不適當である。
- (iv) シックナーの増設が必要であろう。

③PNC 提案の基礎試験に対するインドネシア側の対応

- (i) 浮遊選鉱法による FeS_2 の回収については今回、PNC 主体による基礎試験を希望する。
- (ii) $\text{Ca}(\text{OH})_2$ 添加による SiO_2 の共沈試験については、Control analysis グループにて対応する。

④試験実施に伴うPNC よりのコメント

- (i) 浮遊選鉱法についてはPNC の持参した捕集剤等を用いて FeS_2 の回収試験を実施すると同時に鉱石中の硫化モリブデン(MoS_2)の回収についても試みる。
- (ii) $\text{Ca}(\text{OH})_2$ 添加による SiO_2 の共沈試験については、浸出液を現地より輸送して試験を行うのではなく、輸送中に液の状態が変化していくことを考慮して必ず、試験室にて浸出液を作成して試験を実施すること。

(4) 精製工程

①インドネシア側の問題点

- (i) 連続イオン交換塔の自動化を図りたい。
- (ii) SiO_2 の影響を受け、運転が中断する。
- (iii) イオン交換塔の材質を強固なものに交換したい。
- (iv) PNC が使用しているフィルターの仕様について知りたい。

②検討結果

- (i) 連続イオン交換塔の自動化については、日本では、污水处理システム等での実績があり、経済的余裕があれば、自動化は容易である。
- (ii) SiO_2 の影響を排除するために、前工程にて SiO_2 の除去法について検討を重ねてきたが、本工程を溶媒抽出法に切り替えることもその一法であるように考えられる。
- (iii) イオン交換塔の材質はFRP 製にすることにより、化学的、物理的及び機械的強度が増し、また、製作も比較的容易であり、価格も安価である

(二) PNC が使用しているフィルターの仕様は、表－3 の通りである。

表－3 カートリッジフィルターの仕様

名 称	数量	項 目	仕 様
カートリッジフィルター	1 基	型 式	円筒型
		容 量	0.04m ³
		材 質	SS41/HRL製
		寸 法	φ 300 × H 550 (直胴)
		エレメント	10 μ - φ 65×500 L

(5) 沈殿・乾燥工程

①インドネシア側の問題点（特になし）

(イ) PNC が使用しているイエローケーキ乾燥炉について知りたい。

(ロ) PNC がUF₄ 乾燥用に用いている乾燥機について知りたい。

②回答

(イ) PNC が使用しているイエローケーキ乾燥炉は、multi-stage furnance であり、
運転温度は、約300 ℃である。

(ロ) PNC がUF₄ 乾燥用に用いている乾燥機は、振動流動型乾燥機である。

(6) まとめ

センターの情報から見て、現在のパイロットプラントのウラン回収率の低さ(50 ～60%)
は、製錬の基礎試験が不十分なままでパイロットプラントを建設したことにあると考えら
れる。従って、センターにとって必要なことは、先ず、現在生じている問題を解決するた
めの基礎試験データの取得が必要となる。そのため、

(イ) 将来に商業採掘されると予想される鉱石と同じ新鮮なcomposite 鉱石を採取する
こと

(ロ) それを用いて詳細なテストを行うこと。得られたサンプルの分析は完全に行うこ
と。

特に、浸出貴液中のSiO₂が時間と共に固体のSiO₂としてSSとなり、また、沈積
して運転の障害となると言っているので、その問題を解決するための基礎データ
の取得が重要であろう。

パイロットプラントで処理しているものと類似の鉱石をカナダ等では商業的に処理してイエローケーキを製造している（付録－１及び２参照）。従って、インドネシアでも基礎からしっかりとデータを積み上げていけば経済的にイエローケーキを製造できる。

7.5.3 基礎試験について

(1) 基礎試験概要

今回の研究交流においては、ウラン鉱石中の FeS_2 及び MoS の回収を行うためにセンター所有の浮選機を用いて FeS_2 及び MoS の浮遊選鉱基礎試験を実施した。

浮選に係る試薬及び備品については、前回の調査によりインドネシアでは入手困難であることがわかっていたので今回の研究交流に当たりPNCより持参した。付録－４にPNC持参試薬等リストを示す。なお、試薬以外に試薬添加用注射器(5ml用)20本を持参した。

(2) 基礎試験内容

① 目的

カリマンタン産ウラン鉱石中の FeS_2 及び MoS の回収を浮遊選鉱にて行うための基礎的データを取得することを目的とする。

② 試薬及び装置

(1) 試薬

(i) 捕集剤

- ・ SN-B
- ・ NKY 120-T
- ・ NKY 260

(ii) 気泡剤

- ・ NKY Pine oil No.10

(iii) pH調節剤

- ・ 硫酸(H_2SO_4)
- ・ 塩酸(HCl)
- ・ 水酸化ナトリウム(NaOH)

(ロ) 装置

デンバー型浮選機（センター既設の機器（詳細不明））

③方法（付録－3 参照）

- (イ) パルプの調整：一定粒度に粉碎したウラン鉱石を必要量量り取り，一定量の水を添加してパルプを作成する。（本試験のパルプ濃度は（鉱石重量／水重量）にて決定する。）
- (ロ) 試薬の調整：各試薬を必要量量り取り，一定濃度に希釈する。（希釈不要な試薬もある。）
- (ハ) 予備攪拌：パルプを浮選機のベッセル（3 ℓのベッセル使用）に入れ，空気を導入せずに予備攪拌を行う。この時，設定濃度にpHを調節すると共に，必要な試薬を添加する。
- (ニ) 浮選試験：試料の調整が終了したら，ベッセル内に所定量の空気を導入する。気泡が形成し始めたら備付けのスクレーパにより気泡をかき取る。特別な試験以外は，かき取り時間を5～10分とする。優先浮選等の試験時には，一回目の浮選終了後，時間とpH値を測定し直ちに，必要試薬を追加し試験を継続する。
- (ホ) 試験終了：浮選試験終了後，攪拌を停止し，時間及びパルプのpH値を記録する。
- (ヘ) 分析：浮選により回収した試料については，ろ過，乾燥し，重量測定の後，構成元素の定量分析を行い，回収率等を求める。

④今回の試験内容

- (イ) FeS_2 及び MoS に対する各捕集剤の浮選効果試験
- (ロ) 各pH値における FeS_2 及び MoS の浮選状況確認試験
- (ハ) 適正浮選時間確認試験
- (ニ) 捕集剤及び気泡剤等の組み合わせによる浮選効果の確認試験
- (ホ) FeS_2 及び MoS に対する優先浮選試験

⑤ 試験結果

本試験の結果については現在解析中であり、詳細については、第2報にて報告する。

⑥ 試験後の感想

(イ) センターでは、試験を実施するための試薬、機材が不足しているために、本件を継続していくためには、なんらかのバックアップが必要である。

例えば、浮遊選鉱試験を行うに当たり、少なくとも、

- (i) 純水製造装置一式
- (ii) PHメータ及び同機器のメンテナンス用品一式
- (iii) 各種電子天秤（センターに1台はあるが貴重品扱いである）
- (iv) マイクロピペッター一式
- (v) メスフラスコ等精密ガラス器具一式

が必要であり、また、ベッセル容量の小さい小型浮選機1台あった方が試験が行い易い。

試薬については、自国内での入手が困難な物品が多いようであるので、隣国のシンガポール（飛行機で1時間の距離）より入手できる体制をとればよいと思われる。今回の研究交流にあたり、とりあえず、シンガポールから入手経路は確保した。しかしながら、試薬や装置類のみを整えても、十分な分析を遂行できる体制ではないため以下に示す分析機器も必要と考えられる。

- (i) 電位差滴定装置（高濃度ウラン分析用）
- (ii) 温度滴定装置（ U^{+} 、 U^{4+} 、 SO_4^{2-} 分析用）
- (iii) 原子吸光分光分析装置（YC～UF₆ 中の不純物元素分析用）
- (iv) ICP 発光分光分析装置（YC、UF₄、UF₆ 中の不純物元素分析用）
- (v) 蛍光X線分析装置（元素の定性、定量分析用）

(ロ) センターには十分な人材は揃っているが、上述のごとく、必要機材や試薬の入手が困難な状態にある。センターにとってウラン製錬で経済的に高いウラン回収率が得られることが（現パイロットプラントでは低い回収率しか得られていない）、最も重大なことであるが、上述のように設備や薬品が不足していて十分な基礎試験ができていない。従って、センターから1～2名の技術者が研究交流の留学生として人形峠事業所に来峠し製錬試験を行い、得られた基礎データから十分に製錬に対し確信を持たせることが、日本として有効な技術的援助の一つであると考えられる。

7.5.4 その他の技術的検討

(1) liquid membrane について

センター：liquid membrane についての情報を知りたい。

PNC：人形峠事業所や日立製作所(株)における実施概要及び磷酸からのウラン回収試験について述べ、また、基礎試験方法の概略について説明を行ったが、詳細については、後日資料を送付することとした。

(2) 分析技術について

センター：以下の分析技術についての情報を知りたい。

- ・ 鉱石中のウラン測定法
- ・ イエローケーキ中のウラン測定法
- ・ 浸出液中のウラン測定法
- ・ 砒素測定法
- ・ 鉱石中の磷酸(PO_4) 測定法
- ・ バナジウム測定法
- ・ ジルコニウム測定法
- ・ 第一鉄イオン測定法
- ・ 第二鉄イオン測定法
- ・ 全鉄量測定法
- ・ 鉱石中の珪素測定法
- ・ 浸出液中の珪素測定法
- ・ 分光光度計によるフリー硫酸測定法
- ・ 分光光度計による全稀土類量測定法
- ・ 分光光度計による各稀土類量測定法
- ・ 分光光度計による珪素測定法
- ・ 分光光度計によるモリブデン量測定法
- ・ 分光光度計による鉱石中の硫黄量測定法
- ・ 分光光度計によるトリウム測定法

PNC：既知のデータについては、後日マニュアル等を送付する。

(3)機器・試薬等について

センター：以下の項目についての技術情報を得たい。

- ・遠隔操作ができる混合機
- ・シックナー内スラリー用レベル計
- ・イエローケーキ用乾燥機
- ・ドラムフィルター及び水平式フィルターの設計に関する資料
- ・ウラン浸出液よりの珪素及びモリブデンの除去法
- ・ウラン浸出液ろ過用ろ過剤
- ・回転計に関する資料
- ・過塩素酸鉛($\text{Pb}(\text{ClO}_3)_2$)に関するデータ

PNC：本項目の中には既に回答済のものもあるが、入手可能な情報については、後日連絡する。

センター：以下の項目についてセンターでの入手が困難であるのでPNCの協力を期待する。

- ・分光光度計用タイゴンチューブ（約2m）
- ・凝集剤 Accofloc A-110
- ・凝集剤 Accofloc A-130
- ・TNOA
- ・Span-80
- ・Unicellex-50
- ・Peristaltic(plastic pipe):1.2mm ϕ ×0.8mm ϕ ×25m^L（タイゴンチューブで可）
- ・マイクロピペッター一式
- ・稀土類元素抽出用溶媒

PNC：各種必要物品については、PNCに持ち帰り善処する。また、担当者レベルで入手可能な物件については、帰国後送付する。さらに、試薬等の購入経路については、シンガポールのメーカーと連絡をとりつつ開拓していく。

8. まとめ

昨年に第1回の粗製錬に関する研究交流をインドネシア共和国と行い、センターの粗製錬の問題点に関する知見を多く得ることができた。

例えば、

- (1)ウラン浸出液中の不純物（珪素やモリブデン）の問題
- (2)多量の硫酸や酸化剤を消費する問題

(3)全ウラン回収率が低い問題

等を挙げることができ、また、機器・装置類が十分ではなく、また、老朽化が進んでいることをみることができた。現状の機器や装置のみで考慮した場合、今回の研究交流では、センターの抱えているそのような問題点を一つでも克服するために、センター技術者と粗製錬の各工程に関する問題点の摘出と解決のための討論を十分に行い、各問題に関する解決策を提案することができた。しかしながら、現状の機器や装置のみで考慮した場合、センターが協議した結果を基礎試験やパイロットプラント試験に直ちに反映できるか、センターにおける疑問に思われる。

また、センターに浮遊選鉱に関する専門技術者がいなかったため、本研究交流では、PNC が各種浮選用試薬を持参し、主としてウラン鉱石中の硫化鉄と二硫化モリブデンの回収試験を実施して浮遊選鉱の基礎試験方法について指導を行った。試験結果については、センターに十分な分析機器がないということでPNC がサンプルを持ち帰り、日本で分析することにした。

さらに、センターが、試薬や物品関係について十分な取引経路を確立していないようでありかつ、満足のいく予算も獲得していないようであるので、担当者レベルで入手可能な簡単な物品やカタログ類については可能な限りPNC も協力することを約束し、浮選用試薬については、シンガポールのメーカーと相談し、センターが入手可能な状況になった。（付録－8 参照）

ここまでは、研究交流の担当者レベルで実施可能であるが、今後の研究交流に対し、以下のことを提案する。

- (1) 研究交流が今回限りで中断することがなく、インドネシア共和国の製錬事業が軌道に乗るまで今後もバックアップを継続すること。（インドネシア共和国で経済的な製錬工場を建設し、運転をすることはセンターの最も重要な目標である。）
- (2) バックアップについては、技術的バックアップはPNC として当然のこととして、さらに、試薬、装置類（特に分析装置から）も考慮に入れること。
- (3) 研究交流にあたり、インドネシア共和国からの技術者の受入れ*を行い、センターの技術者が十分な環境の下でデータ取得ができるように、PNC の設備を提供する。

他にも検討しなければならない項目は多くあるが、研究交流を円滑に推進していくためには、徐々に先方の分析装置を主体とする研究開発体制を改善していく必要があると考えられる。

*研究交流に際し、センターは、1992年度にKosim Affandi 課長とPaizal Riza 氏の2名の受入れを希望しており、また製錬の問題を解決する上で、この2名の留学は最適であると考えられる。

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5th March, 1990

Extraction of Uranium from Refractory Uranium Minerals

S. Hirono

The number of the minerals containing uranium will be approximately 200. However, the number of uranium minerals mined for uranium milling are surprisingly few. Those are mainly uraninite (pitchblende), coffinite and brannerite. The mineral formulas of those minerals are as follows: uraninite $\{(U^{4+}, U^{6+})O_{2+x}\}$, coffinite $\{(USiO_4)_x(OH)_x\}$, and brannerite $\{(U, Ca, Fe, Th, Y)(Ti, Fe)_2O_8\}$.

The uranium solubilities of those minerals for leaching decrease in order of the above minerals, and brannerite is known as a refractory mineral for leaching.

Brannerite associates often with davidite (ideally $FeTi_3O_8$) which is also the refractory mineral. Both minerals may contain uranium in both the tetravalent and hexavalent form in association with titanium, iron, and occasionally vanadium, thorium, and rare earths.

There are uranium-niobium containing minerals, euxenite, fergusonite, betafite, and pyrochlore as the more refractory minerals, however, those minerals would be rarely used for milling because of small productions as well as the refractory.

The ore including brannerite has been treated economically in several mills.

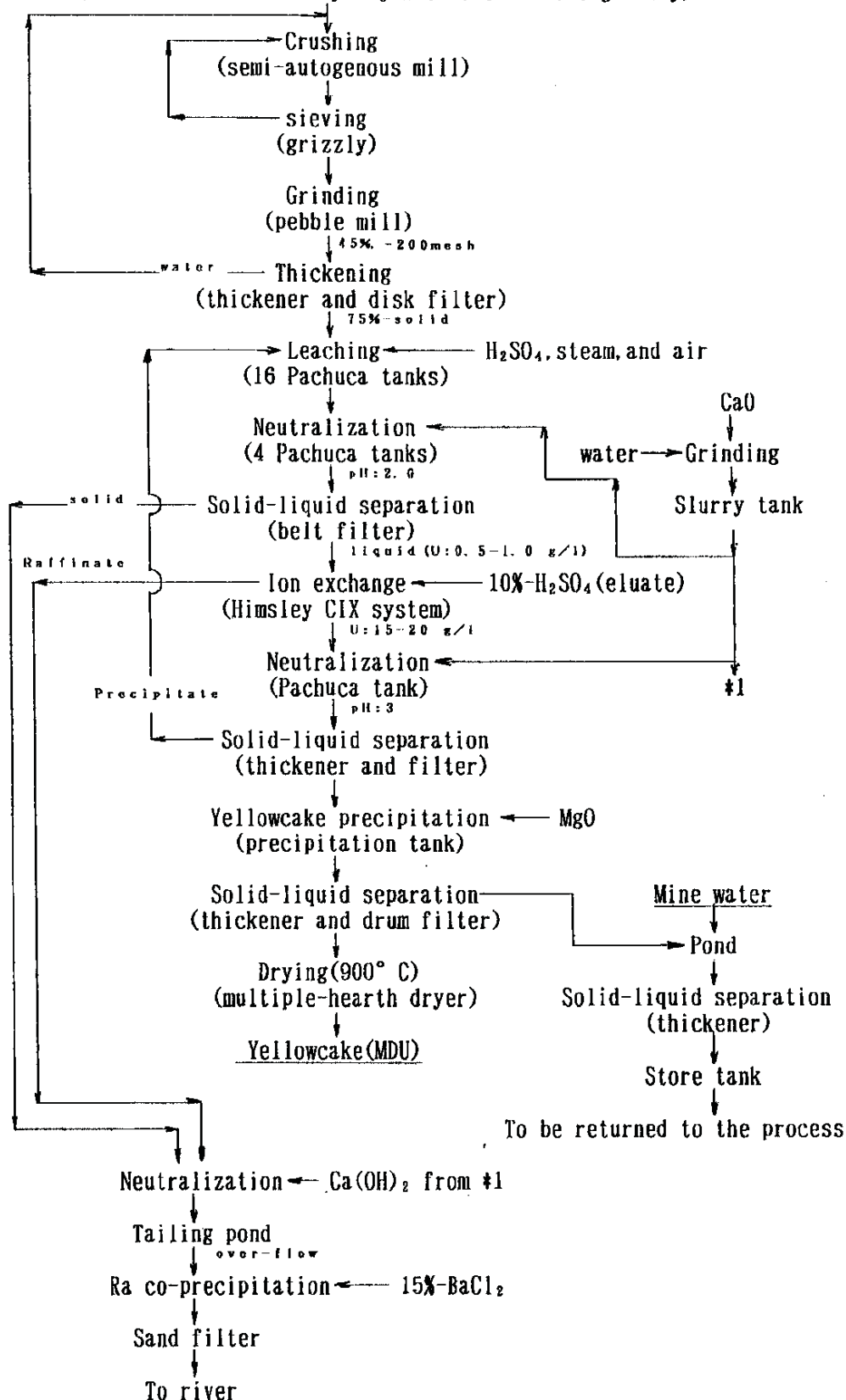
Rio Algom Mines Limited, Stanleigh mill, in the Elliot Lake district of Canada, will be mentioned as a representative example.

(a) Mineralogy

The uranium minerals in the ore are principally brannerite with lesser uraninite and minor amount of uranothorite, thucolite, coffinite and gummite. Monazite is relatively plentiful. Mineralization is mainly within the matrix in quartz-pebble conglomerate and consist of pyrite with minor amounts of apatite, zircon, rutile and leucoxene. In addition there are some silicates such as chlorite, sericite, and feldspar.

Fig. 1. Flowsheet of Stanleigh Milling Process

Ore(0.1%-U₃O₈. Main uranium minerals:brannerite and uraninite)
(The ore was crushed by a jaw-crusher in the gallery)



Rio Algom Mines Limited possesses Stanleigh, Quirk, and Panel mines in the Eliot Lake district, and the mineralogies and features of those ores are quite similar. Therefore, the milling processes treating those ores are nearly similar.

Table 1. Process conditions

<u>Leaching</u>	<u>Uranium concentration</u>
Grain size: 45 % -200 mesh	Concentration process: Himsly CIX
Leaching process: 16 Pachuca tanks in a series	Ion exchange resin: strong base (Amberlite)
Pulp density: 75 % -solid	Eluate: 10 % H_2SO_4
Sulphuric acid: 36 kg/t-ore	Uranium concentration in the solution eluted: 15-20 g/l
Oxidant (air): 350 CFPM/Pachuca tank	<u>Yellowcake precipitation</u>
Leaching time: 30-48 hr	Precipitation process: 2 stages
Leaching temperature: 80° C	First stage: The pH is adjusted to 3.0 by adding lime. The precipitate is separated with thickener and filter.
Uranium recovery: 94 %	Second stage: Magnesium diuranate is precipitated by adding MgO to pH 7.
<u>Solid-liquid separation</u>	<u>Drying</u>
The slurry is separated after neutralization up to pH: 2.	Drying process: multiple-herth dryer
Separation process: belt filter	Temperature: 900° C
Uranium concentration: 0.5-1.0 g/l	
Suspended solids: 5 ppm	
Uranium recovery: over 99 %	

(b) Comminution

At Stanleigh mill (5000 t-ore/day) as shown in Fig. 1, the ore is ground up to 45 -50% minus 200 mesh. Australian ores including brannerite and/or davidite require also grinding to between 55 and 65 % minus 200 mesh size to obtain satisfactory uranium extraction recovery for acid leaching.

However, overgrinding may result increased pulp viscosity, thus adversely affecting uranium extraction rate, and slow settling rate in thickener of solid-liquid separation system.

(c) Preconcentration and leaching

Flotation may be applied to the separation of the sulphides in the ore.

Typical conditions for leaching to achieve 95% recovery are summarized in Table 1.

The neutral slurry is thickened and filtered up to 75%-solid. Approximately 36 kg- H_2SO_4 /t-ore is added to the slurry of 75%-solid, and the free H_2SO_4 concent-

ration is maintained approximately 1N. (Concentrated H_2SO_4 must be added in the slurry in order to maintain approximately 1N free acid, because the specific gravity of the ore is 2.7). Steam is injected to achieve the temperature at 80 ° C. The leaching time requires 30 to 48 hr.

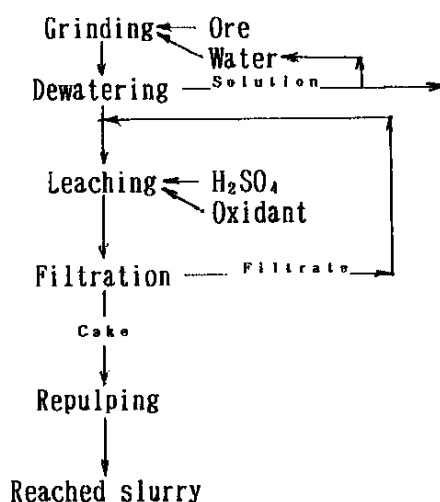
Those conditions in the leaching process are relatively drastic. Depend on the property of ore and further the relatively drastic leaching conditions, the leaching solution may contain a large amount of silica. The silica dissolving or suspending in the solution may have considerably harmful effects to the following processes.

The dissolved silica present in the feed solution is thought to occur the problem of slow-breaking dispersion within the settler or mixer-settler. Silica concentrations less than 0.7 gram per liter do not cause difficulty, but above this value may lead to the formation of stable emulsions in aqueous continuous systems. Organic-continuous systems are less affected by dissolved silica even at concentrations of up to 2.5 gram per liter. Semi-permanent emulsions may be formed at the interface when fine solids are present in amine-type systems, leading to solvent losses and, in extreme cases, to the necessity for shutting down the operation for cleanout. ¹⁾

Silica acts as resin poison. Silica exists in acid solutions primarily in non-ionic soluble form when the pH is less than 4 although some reactive ions are apparently present. Such silica in solution may form weak complexes with the anion present on the resin; with an increasing tendency to do so in the order $\text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{--}$. In either ion, an increase in pH is characteristic of the anionic resins as a result of the Donnan membrane effect. Water washing which will remove H^+ ion from adsorbed HSO_4^- ion on the resin will raise pH within the resin, and further increase the formation of precipitated silica. Once formed inside the resin bead, precipitated silica blocks the resin pores to cause decreased reaction rates. The silica content of the resin may increase to as high as 8 to 10 percent if not controlled, and within this range may cause the resin to fail through rupture of the resin crosslinks. ¹⁾

At the leaching of Stanleigh ore, the relatively high concentration of free acid remains in the leached solution. The recycle circuit as shown in Fig.2 was installed in several of the Canadian mills in the Elliot Lake area where free acid concentration of up to 50 grams of H_2SO_4 per liter were needed for treatment of ore containing the relatively refractory mineral, brannerite. In a modification of the circuit a portion of the final leach slurry was recycled to assist in the oxidation due to the contained ferric iron. However, the application must be investigated thoroughly because of the added capital cost for the extra stage of filtration and to the cost of operating and maintaining this equipment.

Fig.2 Recycle circuit of leaching



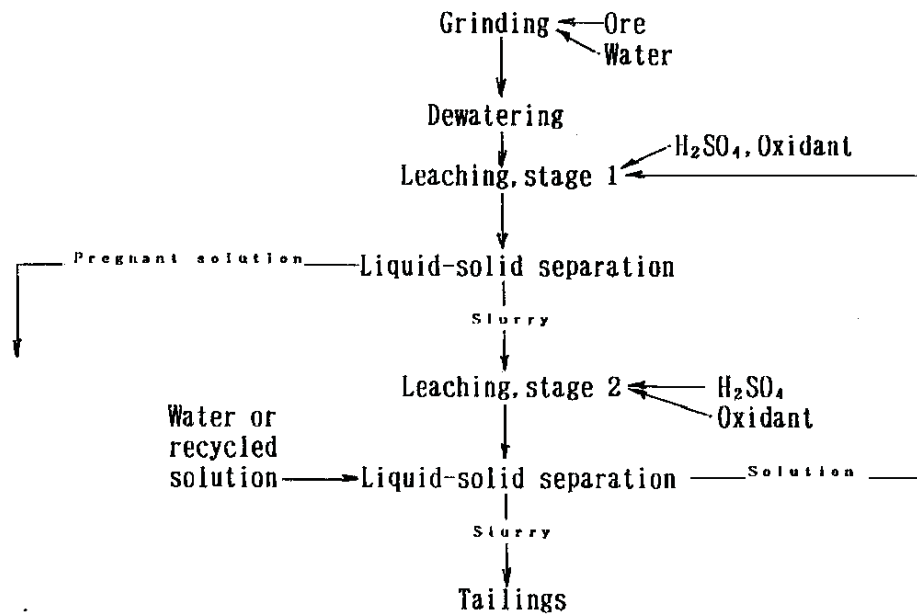
For the ore which more severe leaching is required, the leaching of two stages as shown in Fig.3 may be used. The economic investigation would be needed also for the application of the system.

The presence of sulphides in ore should suggest that bacterial leaching be examined. Bacterial leaching of low-grade ore including sulphides in vat may be effective particularly in the tropics.

(d) Solid-liquid separation

The pH of the slurry from the leaching process at Stanleigh mill is adjusted to 2 with adding of lime, and then the slurry is filtered with belt filter.

Fig.3 Two stages leaching



At Rio Algom-Panel, drum-filters are used, and Rio Algom-Quirke have a 4-stage cyclone and circuit-washed sands separated join washed slims from a 6-stage CCD circuit using Enviroclear thickeners, at the neutralization pachuca prior to tailings disposal.

In solid-liquid system, washing water is added to wash slurry, and the increase of the pH of slurry may result in uranium loss. This loss attributes to reprecipitation depending on the reaction of uranium and inorganic acid anion such as arsenic acid anion or phosphoric acid anion, to adsorption on clay, such as montmorillonite, or on carbonaceous materials having ion exchange properties, or to the presence of uranium silicates or other refractory type minerals present in small amounts. In case of those, acid would be added in the slurry to maintain the pH under 1. Table 2 shows the pH ranges in which various anions may precipitate uranium from sulphate solutions.

Table 2. pH range for precipitation of uranyl or uranous ion with various anions in sulphate solutions¹⁾

		pH range		
		Hydroxide	Phosphate	Arsenate
Uranyl		3.8-6.0	1.9-2.5	1.3-1.7
Uranous		2.5-6.0	<1.2	<1.2
				Carbonate
				3.5-6.0
				—

(e) Concentration and purification

The clarified leach solution contains uranium of 0.5 - 1.0 g/l. The suspended solids in the solution are as few as 5 ppm. Continuous ion exchange apparatus is used, and uranium of 15 - 20 g/l is eluted with 10%-sulphuric acid eluant.

There are significant quantities of thorium and lanthanide in the liquors produced at several mills in the Elliot Lake area. Table 3 shows typical liquor analyses.

Table 3. Typical liquor analyses(g/l)²⁾

	Acid free	U ₃ O ₈	Th	SO ₄	NO ₃	Rare-earth oxides
Leach discharge	41	4.61	0.97	103.2	1.08	0.89
Pregnant liquor	0.9	1.02	0.14	18.1	0.79	0.18
Barren liquor	0.7	0.0011	0.15	18.9	1.24	0.23

These elements can cause some problems in the subsequent treatment by being extracted in small but significant proportions with the uranium and by causing specifications to be exceeded for these elements. However, when these are recovered economically, these will be produced as by-product.

The presences of polythionates and ionic silica in liquor would result in resin poisoning problems and it is believed to be aggravated when chloride elution was used. The most part of the poisoning problems on silica in liquor are mentioned on page 4.

Comparison of the Stanleigh plant, Canada with the Kalan pilot plant, Indonesia is shown in Table 4, and the reasons and improvements inferred on the low uranium recovery at Kalan pilot plant are shown in Table 5.

References

- (1) Robert C. Merritt, The Extractive Metallurgy of Uranium, Colorado School of Mines Res. Inst. 1971.
- (2) International Atomic Energy Agency, Significance of Mineralogy in the Development of Flowsheets for Processing Uranium ores (Technical Reports Series No. 196), IAEA, Vienna (1980).

Table 4. comparison of Stanleigh plant and Kalan pilot plant

	Stanleigh process Canada	Kalan pilot plant Indonesia
<u>Ore</u>		
Uranium content(U_3O_8):	0.1%	0.1%
Uranium mineral:	Brannerite, uraninite, urano- thorite, thucolite, coffinite	Uraninite, brannerite
<u>Leaching</u>		
Ore grain size:	45% minus 200 mesh	100% minus 48 mesh
Leaching process:	16 Pachuca in a series	4 mixing-tanks in a series
Pulp density:	75%-solid	50 - 60%-solid
H ₂ SO ₄ addition:	36 kg/t-ore	125 kg/t-ore
Oxidant addition:	Air, 350 CFPM/Pachuca	MnO ₂ , 20 - 30 kg/t-ore
Time:	30 - 48 hr	8 hr
Temperature:	80 ° C	60 ° C
Uranium recovery:	94%	about 70(60 - 80)%
<u>Solid-liquid separation</u>		
Separation process:	Belt filter	4 thickeners in a series
Uranium concentration:	0.5 - 1.0 g/l	—
Suspended solids:	5 ppm	—
Uranium recovery:	over 99%	—
<u>Ion exchange</u>		
Exchange process:	Himsly SIX	8 fixed columns in a series
Ion exchange resin:	Amberlite(strong base)	Amberlite(IRA 400)
Eluant:	10%-H ₂ SO ₄	1.5 M-NaCl
Uranium concentration:	15 - 20 g/l	—
<u>Yellowcake precipitation</u>		
Precipitation process:	2 stages precipitation 1st stage:Ca(OH) ₂ , pH:3 2nd stage:MgO, pH:7	2 stages precipitation 1st stage:Ca(OH) ₂ , pH: 3.5 2nd stage:MgO, pH:7.0 - 7.5
<u>Total uranium recovery:</u>	over 92%	50 - 60%

Table 5. Reasons and improvements inferred on low recovery of uranium at Kalan pilot plant

<u>Reason</u>	<u>Improvement</u>
(1) Brannerite in the Kalan ore may have more refractory property for dissolution in acid than that in other ore.	(1) The property should be ascertained by mineralogical and leaching tests.
(2) The grain size(100% minus 0.3 mm) of the ore would be relatively coarse.	(2) The leaching tests should be carried out with the ore samples ground up to minus 200 mesh(0.074 mm).
(3) The pulp density(50 - 60%-solid) would be relatively low.	(3) The pulp density should be increased. it will result in increase of acid concentration.
(4) The leaching time(8 hr) would be relatively short.	(4) The leaching tests under longer leaching time such as up to 50 hr would be carried out.
(5) The leaching temperature(60° C)	(5) The leaching test under higher leach-

Table 5(Continued). Results and improvements on low recovery of uranium at Kalan pilot plant

<u>Reason</u>	<u>Improvement</u>
would be relatively low.	ing temperature would be carried out.
(6) The amounts of sulphuric acid and oxidant(MnO_2) added are considerably large.	(6) Small amounts of sulphuric acid and oxidant should be added for leaching tests, and the optimum condition including many other factors mentioned above should be obtained.
(7) The solid-liquid separation has difficult problems.	(7) It should be investigated to adding of cyclons and/or filters and to increasing the stages of thickeners.
(8) The economical and metallurgical considerations would be insufficient.	(8) The instruments and flows in each process should be improved and changed to increase the uranium recovery on the basis of economics; beside, the improvement increasing the uranium recovery through all process would be investigated.

Uranium mills treating brannerite ores

Introduction

The Uranium mills which have or had treated the uranium ores containing brannerite are generally as shown in Table 1.

Table 1. Uranium mills which have or had treated brannerite ore

Country	Name	Comminution	Leaching
Canada	Denison	80% minus 65 mesh (50% minus 200 mesh)	Conventional acid leach in air agitation pachucas. Sodium chlorate, 65-75°C, 40 hours
Canada	Kerr Addison -Agnew Lake	No milling	Acid in-situ leach
Canada	Rio Algom -Quirke	80% minus 65 mesh (50% minus 200 mesh)	Conventional acid leach in air agitation pachucas. Only oxygen from air. 65-75°C. 40 hours.
Canada	Rio Algom -Panel	80% minus 65 mesh (50% minus 200 mesh)	Conventional acid leach in air agitation pachucas. Only oxygen from air. 65-75°C. 40 hours.
Canada	Preston Mines -Stanleigh	80% minus 65 mesh (50% minus 200 mesh)	Acid leach in air agitation pachucas. Only oxygen from air. 80 °C. 40 hours. (Pre-aeration after grinding).
South Africa	Anglo-Vaal Reefs	7% plus 150 μ , 28% minus 150 plus 75 μ , 65% minus 75 μ	Acid leach in air agitated pachucas. MnO ₂ . 60 °C.
South Africa	Angro-President Brand	6.1% plus 150 μ , 22.3% minus 150 plus 75 μ , 71.6% minus 75 μ	Acid leaching in air agitated pachucas. MnO ₂ . 60-65°C.

Most sulphuric acid leaching plants which treat ordinary uranium ore operate generally under the leaching conditions in lower levels.

The ores containing brannerite require fine degrees of comminutions, high acid

concentration, long retention time, high temperature and oxidizing conditions to effect high extractions, as shown in Table 1.

The comminuting degrees of brannerite ores are the 80% minus 65 mesh (50% minus 200 mesh) in Canada, and the 93-94% minus 150 μ in South Africa (Note: 65 mesh = 208 μ , 200 mesh = 74 μ). The degrees of the comminutions at usual plants are approximately minus 48 mesh (295 μ) in acid leach, and approximately minus 250 mesh (61 μ) in alkaline leach. In the case of the brannerite ore, the degree of comminution lies between those in acid and alkaline leachs.

The acid concentration is high. The concentrations are in the levels of 75 g/L at Denison and approximately 70 g/L at Stanleigh, although 20-50 g/L at usual plant.

The retention time is as long as approximately 40 hours compared with 4-24 hours at usual plant.

The temperatures of 60-80 °C are higher than that at usual plant in which the temperatures of the leach is approximately from ambient temperature to 60 °C.

Air is used entirely as oxidant in Canada with one exception using sodium chlorate along with air in Denison. It is inferred that supplying air into pachuca is effective to oxidize uranium minerals and gangue minerals such as pyrrhotite.

For dissolving of uranium from uranium ore, particularly from brannerite ore, it is very important to contact an oxidant and uranium minerals. In pachuca, it is the important factor improving the uranium extraction that the ore and air are mixed to contact sufficiently numerous and fine air bubbles on the surfaces of the ore grains.

Manganese oxide is used as an oxidant in South Africa.

Autoclave has not been used the dissolution of uranium from brannerite ore, however pachuca has been used widely. It is inferred that pachuca is economical in operation and extracts uranium effectively.

Typical Plants

Denison plant and Stanleigh plant are described as the typical plants treating the ore containing brannerite.

1) Denison plant

Uranium minerals are brannerite, uraninite and monazite. Gangue minerals are quartz, chlorite, sericite, pyrite, pyrrhotite and rutile. The content of pyrite and pyrrhotite is about 7%. The silica content is greater than 75%.

The uranium content in the ore is 0.10-0.15% U_3O_8 in average.

The ore (-18 cm) from underground is crushed and ground to 45-50% -200 mesh. The ground ore is dewatered to 75% solid, and the dewatered slurry is fed to the leaching section.

The leaching section (Fig.1) consists of two parallel lines of eleven pachacas each. The size of the pachuca is as follows:

Diameter: 22-1/2 ft (6.86 m)

Hight: 50 ft (15.24 m)

Bottom: 60° cone

Inside: Lined with rubber

Agitation: By injection of air at 50 psig (3.5 kg/cm²) through three 1-in. pipes located at 27-in. centres in the conical bottom section.

Retention time in the leaching section is usually 36 to 48 hours.

Concentrated sulphuric acid (93%) is added to the first pachuca in each circuit to maintain a free acid level of 75 g/L.

The target of uranium concentration in the solid tail is 0.08 lb/t (36.3 g/t).

Temperature is held automatically at 75 °C by the injection of live steam to the first and third pachucas.

Oxidation-reduction potential is controlled indirectly by air injection and directly by sodium chlorate addition. Air at 450 cfm (12.74 m³/min) and 50 psig (3.5 kg/cm²) is added to the first two pachucas in each circuit to oxidize any

reducing materials. A redox probe in the first pachuca shows wild fluctuation between 100 and 450 mV. Rubber-covered and -lined steam injectors are used in

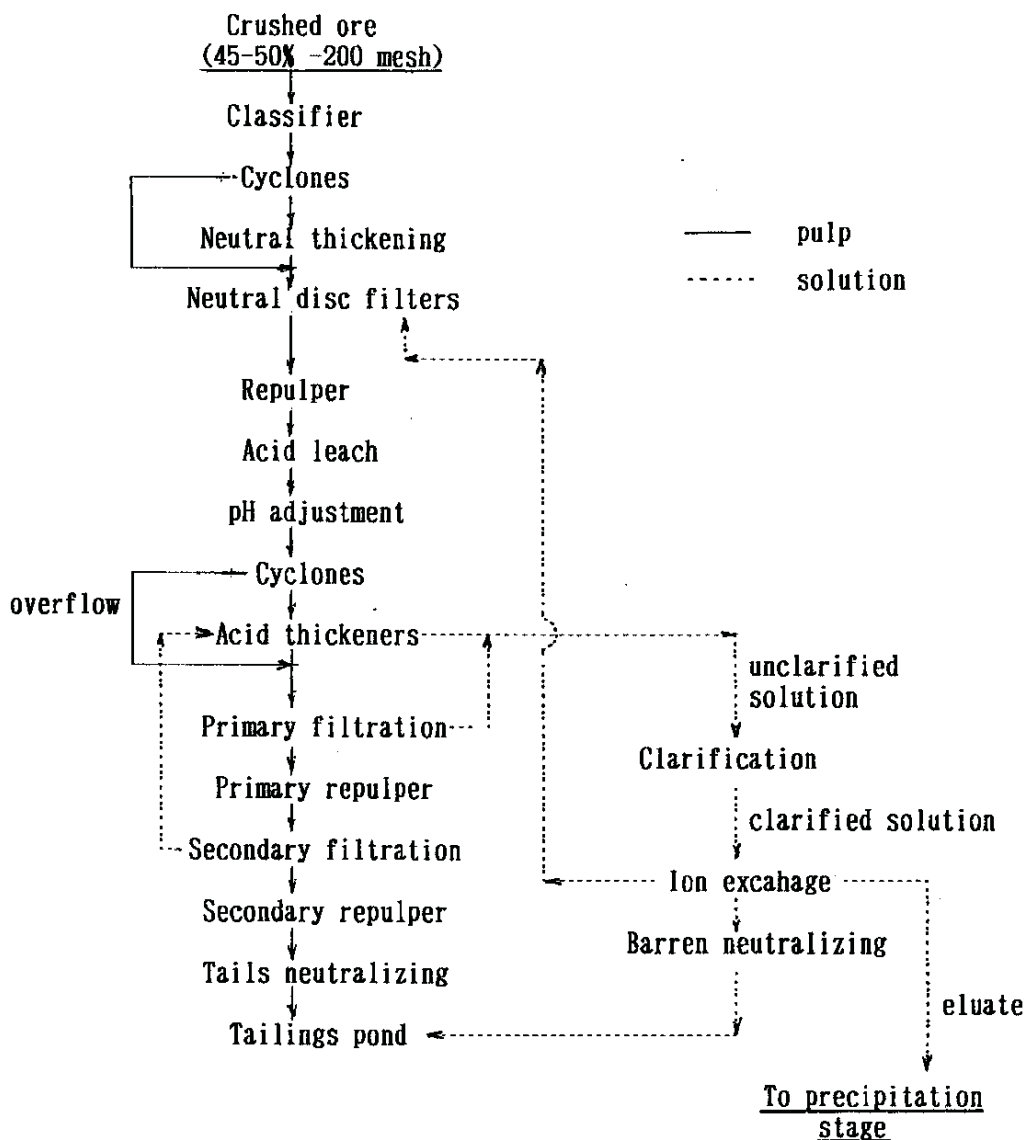


Fig. 1 Leaching section at Denison plant

the first pachuca, because stainless-steel injectors disintegrate in several days under these conditions. The redox potential levels out in the feed to the second pachuca at about 350 mV. Sodium chlorate is added automatically as a 15% solution and the redox is controlled at 450 mV in the second pachuca. Air flow to the last part of the leaching section is controlled at 300 to 350 cfm (8.50

to 9.91 m³/min).

The density control of the pulp is important. High pulp densities result in lower steam and reagent consumptions. However, as the pulp density increases, the air flow decreases, and the redox potential becomes lower. The lower redox potential results in lower extraction. Therefore, densities are controlled at 1.90 (75% solid).

The pH of the leached pulp flow is raised to 2.0 by adding of lime slurry. The pulp is fed to cyclons and thickeners, and is separated to tailings and unclarified solution. The clarity of this solution is generally between 300 and 500 ppm. The solution is clarified by means of filters, and the clarity becomes generally less than 5 ppm.

Clarification is necessary for operating an ion exchange section without channeling of pregnant solution and drop of high pressure across the resin beds.

The ion exchange section consist of moving-bed type columns containing Amberlite IRA 400, a strong base anion exchange resin. Elution is carried out by using 1 N nitrate solution as an eluate. The uranium concentration in the eluate is 20 g/L.

Uranium precipitation is carried as follows:

The pH of the first-stage tank is automatically controlled with lime slurry to regulate the sulphate levels at 35 g/L. The gypsum in the pregnant solution reduces by the pH-control.

Phosphoric acid is added to the second-stage tank to complex thorium, rare earth and titanium.

In the third-stage tank, ammonia is added to control at a pH of 3.5 to precipitate the complexed impurities and iron. The slurry from the third-stage tank is fed to a thickener. The overflow is fed to the fourth-stage tank, and a mixture of ammonia and air is added to a pH of 7. The ammonium di-uranate (ADU) precipitated is washed and dried.

A typical analysis of the yellowcake is given in Table 2.

Table 2. Typical yellowcake analysis(%)

U ₃ O ₈	82.34	ThO ₂	0.90	K	0.25
Ca	0.37	Fe	0.41	PO ₄	0.23
SO ₄	3.92	Ti	0.04	Moisture	1.00

2) Stanleigh plant

The uranium minerals are uraninite, brannerite and monazite. The gangue minerals are principally quartz, sericite, chlorite and pyrite. The uranium content is 0.05-0.10% U₃O₈.

The ore is crushed and ground by a jaw crusher and a semi-autogeneous mill. The degree of comminution is 45% -200 mesh.

The ground ore is dewatered to 75% solid, and the dewatered ore pulp is fed the leach section.

The leach section is consist of two parallel lines of eight pachucas.

The leaching conditions are much the same with those in Denison plant, as follows:

Retention time, temperature and sulphuric acid concentration are 30-48 hours, 80°C and 36 kg/t-ore(72 g/L) respectively.

The uranium extraction ratio is 94%.

The leaching conditions at Stanleigh and Denison plants are shown in Table 3.

The pH of leached pulp is adjusted to 2.0 by adding of lime slurry, and the pulp is filtered. The clarity of the clarified solution is 5 ppm. The uranium concentration is 0.5-1.0 g/L.

The solution is fed the Himsly CIX system in which strong base ion exchange resin is loaded. Uranium adsorbed on the resin is eluted by using 10% sulphuric acid as an eluate. The uranium concentration in the eluate is 15-20 g/L.

The eluate is adjusted at pH of 3.0 by adding lime slurry, and the precipitant is removed.

Magnesium oxide is added in the solution to produce magnesium uranate.

Table 3. Comparison between leach conditions at Stanleigh and Denison plants

	Denison	Stanleigh
Apparatus	Two parallel lines of eleven pachucas	Two parallel lines of eight pachucas
Degree of comminution	40-50% -200 mesh	45% -200 mesh
Pulp density	75% solid	75% solid
Retention time	36-48 hours	48 hours
H ₂ SO ₄ concentration	75 g/L	72 g/L
Temperature	75°C	80 °C
Oxidant	Air and sodium chlorate	Air
Density	1.90 (75% solid)	-

Summary

The ores containing brannerite have and had been treated economically at several mills, particularly in Canada.

However, the leach conditions are more severe than those at the plants treating usual ores. As mentioned above, for recovering uranium from the ores containing brannerite it may be necessary to leach for about 50 hours at 75% solid with 75 g/L of free sulphuric acid using air or air along with sodium chlorate as oxidant at about 80 °C. It may be required that the grain sizes of the ores are as fine as 45-50% -200 mesh (-74μ). Furthermore, a important factor for extracting effectively uranium is to keep the redox potential at or above 450 mV.

In PNC laboratory, the two tests are carried out to leach uranium from the ore containing uraninite and brannerite under the same conditions except for the pulp agitation. At the one test, the pulp was agitated vigorously to be dispersed oxygen injected as an oxidant in a state of fine froth. At the other test, the pulp was agitated with the one third of the former revolution-speed.

The redox potential and uranium extraction ratio of the former were 480 mV and 98%, respectively. Those of the latter were 307 mV and 20%, respectively.

Pachuca is used generally the leach of uranium from the ore containing brannerite. The ore in a pachuca is agitated and oxidized indirectly by air injection. Adequate agitation and oxidation by air is important for the effective extraction of uranium. When the oxidation by air is not unsatisfactory, an oxidation reagent as sodium chlorate or manganese oxide would be added to obtain the oxidizing level of 450 mV.

The density of leach pulp affects the dissolution of uranium; the density is controlled at 1.90 (75% solid) at the leach section in Denison plant.

(S.Hirono)

Development of the Chelate Resins

—Refinig Technique
at Ningyo Toge Works, PNC—

September 1991

NINGYO TOGE WORKS
POWER REACTOR AND NUCLEAR FUEL
DEVELOPMENT CORPORATION

Development of the Chelate Resins
—Refining Technique in Ningyo Toge Works, PNC—

Ichiro YASUDA *1
Masafumi OKAMOTO *2
Ippei AMAMOTO *2

Abstract

It was carried out by the joint research of PNC and Unitika Ltd. to develop the chelate resins which adsorb selectively the impurities in the hydrochloric acid solution dissolving yellow cake.

Unicellex UR-50 (Unitika), one of the chelate resins, fits for the PNC process as the result of these experiments.

A medium-scale facilities which purify uranium solution by using UR-50 was built and it was operated smoothly.

*1 General manager of Uranium conversion development section

*2 Manager of Uranium conversion development section

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1. Introduction

PNC has made the researches to purify a uranium solution prepared by dissolving yellow cake followed by producing uranium tetra-fluoride.

In this paper, the joint research of PNC and Unitika Ltd. on the purification of uranium solution by using chelate resin are described.

The basic researches and the continuous operation of a medium scale facilities had been carried out during 1984 to 1986.

Solvent extraction cannot be applied to the purification of uranium solution produced by dissolving yellow cake in hydrochloric acid. The ion exchange resin which removes minor impurities until the purity required for producing uranium hexa-fluoride is necessary for the purification of the uranium solution made by dissolving yellow cake.

It was found by the basic researches that some specific chelate resins are suitable for the object mentioned above. The medium scale facilities was installed to purify successively the uranium solution by using the chelate resin and was operated smoothly.

2. Medium Scale Facilities

2.1 Outline of Facilities

Figure 1 shows the flow sheet of the chelate refining test facilities.

These facilities are composed of a chelate refining tower(T-201) which was packed by 1m^3 of Unicellex "UR-50", a cartridge filter(F-209) [see photo], and several vessels and pumps as incidental equipments.

The main equipments are shown in Table 1.

2.2 Particular Features of The Chelate Resin Refining

Particular features of the chelate resin refining are compared with the solvent extraction process as follows:

The chelate resin refining process

- is available for the uranium dissolved in hydrochloric acid solution,
- can treat high-concentrated uranium solution,
- can produce the refined solution which does not contain organic solvent although the uranium solution refined by solvent extraction process contains small amount of solvent to remove as a contamination material, and
- has a smaller installation area and a short residence time of supplied solution.

2.3 Operation

A summary of operation of the chelate resin refining test facilities are as below:

- ① adjustment of the pH value of the yellow cake dissolving solution containing impurities by the addition of 10% MgO slurry(the pH value is 1);
- ② removal of a precipitate formed by the pH value control by the cartridge filter;
- ③ adsorption of metal ions as impurities on the chelate resin to refine supplied solution;
- ④ recycle of a few amount of uranium adsorbing on the resin eluted

selectively by 0.3N HCl to the dissolution step;

- ⑤ elution of impurities on the chelate resin 6N HCl and treatment of the impurities as a waste;
- ⑥ when Mo is contained in the eluate abundantly, the eluate is treated after removing Mo by ferric cohesion precipitation method.

3. Experiments

3.1 The items of experiments

- ① the dissolving tests of the different yellow cakes (Niger, Australia, Canada and W. Germany) with hydrochloric acid;
- ② the filtration test of the yellow cake dissolving solution by hydrochloric acid;
- ③ the running test of the different yellow cake dissolving solutions (Niger, Australia, Canada and W. Germany) through the chelate resin;
- ④ the elution test of adsorbed metal;
- ⑤ the cohesion precipitation and filtration tests of the eluate;
- ⑥ the feeding test of the refined solution to the milling pilot plant;
- ⑦ the superior limit test of the load elements from the electrolytic reduction step to the conversion step.

3.2 Test Run

(1) Procedures

The test run procedures were described as below:

- ① dissolving Niger yellow cake containing the greatest amounts of impurities among the yellow cakes which PNC stores by HCl;
- ② filtration of the dissolving solution by a conventional filter;
- ③ the pH value control of the dissolving solution;
- ④ the refining by the chelate resin;
- ⑤ the addition of HCl to the refining solution followed by the steps from the uranyl solution reduction test to UF_6 conversion;

- ⑥ preparation of reagents using the regeneration of the resin reclamation and the regeneration of the resin by using the reagent;
- ⑦ removal of Mo from eluate by the ferric cohesion precipitation.

(2) Results

Several results described below were obtained as the result of the test run. A prescribed refining effect could be obtained and the facilities and sequence had been operated normally.

Small amount of uranium precipitated during adjusting pH value. It was presumed to be caused by an excess of hydrogen peroxide solution added at the dissolving step.

UO₂ crystalized at the first batch in the electrolytic reduction step because of the lacking of HCl. HCl was, therefore, added and the operation was continued. At the second batch, as HCl was added beforehand before operation satisfactory current efficiency was obtained.

This current efficiency and the treatment amount was slightly lower than those of Australia yellow cake treatment. It can be improved by raising the uranyl concentration in the solution.

The molecules of water of crystallization in hydrated UF₄ produced by the fluorination precipitation are 1.1.

Its fluidity index was 90 and the average of the particle diameter was 93 μ m. Those values may be suitable for UF₄.

The UF₄ from the dehydration step was dehydrated completely. Almost same operation results as the conventional operation could be obtained at the conversion, trapping and filling steps. However, the fluidized medium had to be changed because the sign of partial sintering appeared as rapidly depression of a differential pressure.

Reactivity of dehydrated UF₄ was not much different from the conventional UF₄. A specification of elements showed in Table 2 was satisfied.

Good rates of precipitation and filtration were obtained by adjusting the

pH value at the waste eluate treatment step, and the diatomaceous earth was used as a filter aid. There was no problem throughout the whole process.

3.3 Continuous operation

The chelate refining technique is introduced for the purposes of

- ① the removal of sulfur;
- ② the development of substitute method of the solvent extraction method;
- ③ the removal of Fe, Cu and Mo from yellow cake dissolving solution.

The block flow is described in Figure 2. The yellow cake from Niger and W.Germany were treated by the chelate refining.

After treating Niger yellow cake, W.Germany yellow cake was refined by slightly different condition because its quantity of impurities was different from the former one. Different points are described as below:

- ① The pH value of the solution which W.Germany yellow cake was dissolved was adjusted at 1.3~1.7 prior to refine while the pH value of Niger one is adjusted at 0.8 ~1.0. Because W.Germany yellow cake contained more Cu so the pH value was adjusted to the suitable condition to remove Cu.
- ② The waste treatment of the chelate eluate of Niger yellow cake carried out after removing Mo by the ferric cohesion precipitation but W.Germany yellow cake was treated directly without removing Mo because it contained less Mo amount.

The refining efficiency by the chelate resin is shown in Table 3.

Cu, Fe, Mo, V, etc. can be removed by the chelate refining as impurities.

These elements have bad effects on the next step such as a lowering of the current efficiency by Cu or Fe at the electrolytic reduction step or a formation of volatile fluorides associating with UF_6 at the conversion step.

On the other hand, removal of other impurities by the chelate refining is not anticipated but they can be removed efficiently at the fluorination step.

Uranium of 107.8 tons was treated during the operation of 399.5 hours.

Uranium adsorbed on the chelate resin was a small amount and the uranium was eluted selectively by 0.3N HCl and supplied in the dissolving tank. And impurities adsorbed on the chelate resin was eluted by 6N HCl and the eluate was treated at the waste treatment step. Niger yellow cake containing more Mo was treated after removal of Mo by the ferric cohesion precipitation because only Mo was adsorbed on the waste treatment resin (UR-3100) and the effects on resin become worse.

Some Mo which could not be eluted by HCl and remained on the resin should be eluted by NaOH. The resin was rinsed every time 20t-U treatment of Niger

yellow cake were treated and only one elution was needed after whole W. Germany yellow cake were treated. NaOH solution was treated after the ferric cohesion precipitation.

4. Conclusion

The results of the basic experiment and the operation of the medium-scale facilities are mentioned below:

- ① The chelate refining using UR-50 under hydrochloric acid condition is available for any district yellow cake the same as sulfuric acid condition. The chelate resin is useful for such impurities as Mo, V, Fe and Cu.
- ② Similar results as the basic experiment could be obtained from the experiment by the engineering scale facilities.
- ③ The satisfactory UF_6 agreeing with the UF_6 specification was obtained by using Niger yellow cake solution dissolved in hydrochloric acid.

The full-scale operation of the chelate refining was carried out from March '87 because of the good results obtained in earlier experiments.

Filtrate of
Dissolving Solution

H₂O₂, 10%MgO Slurry

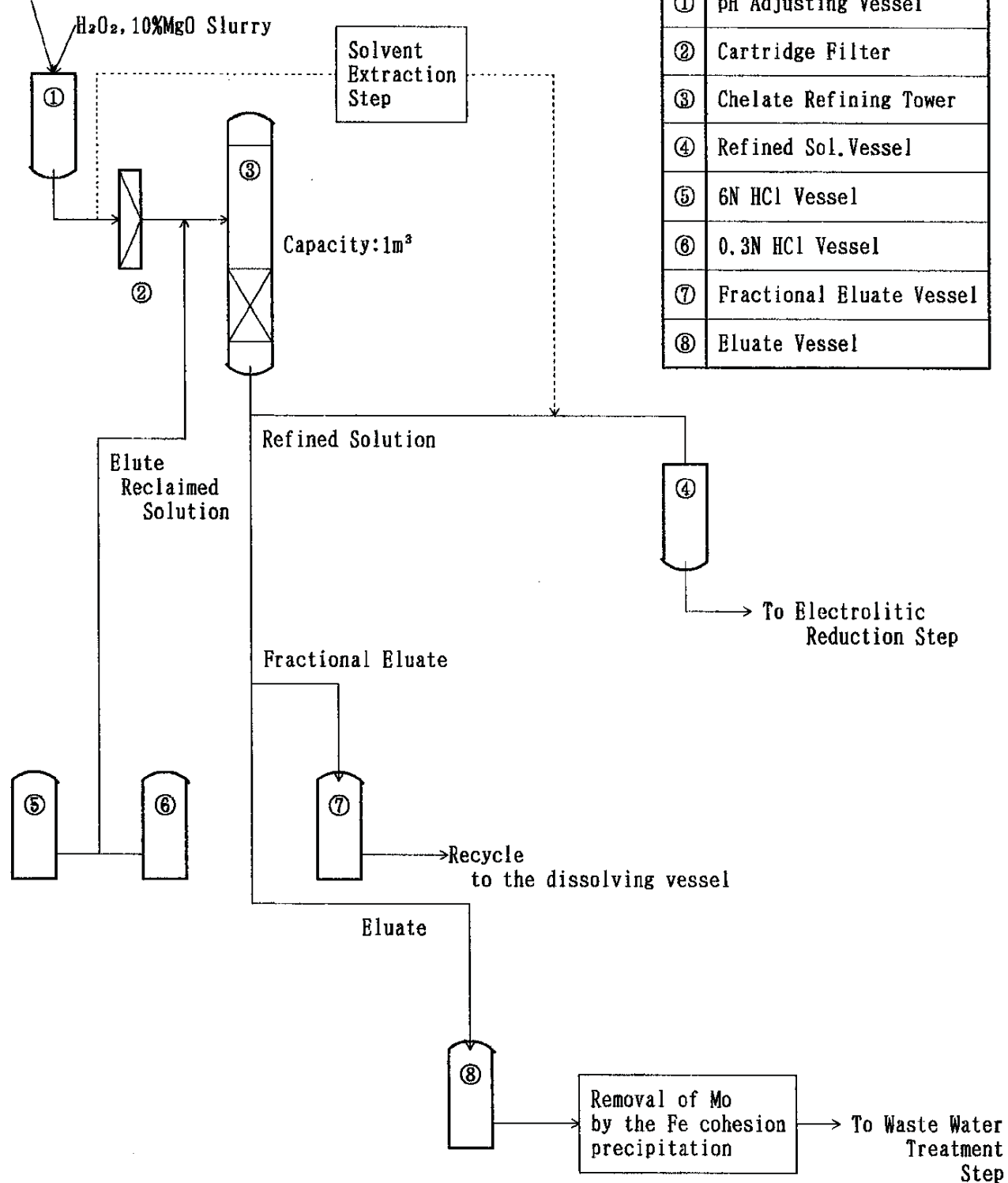


Fig.1 The main flow sheet of the chelate resin refining test facilities

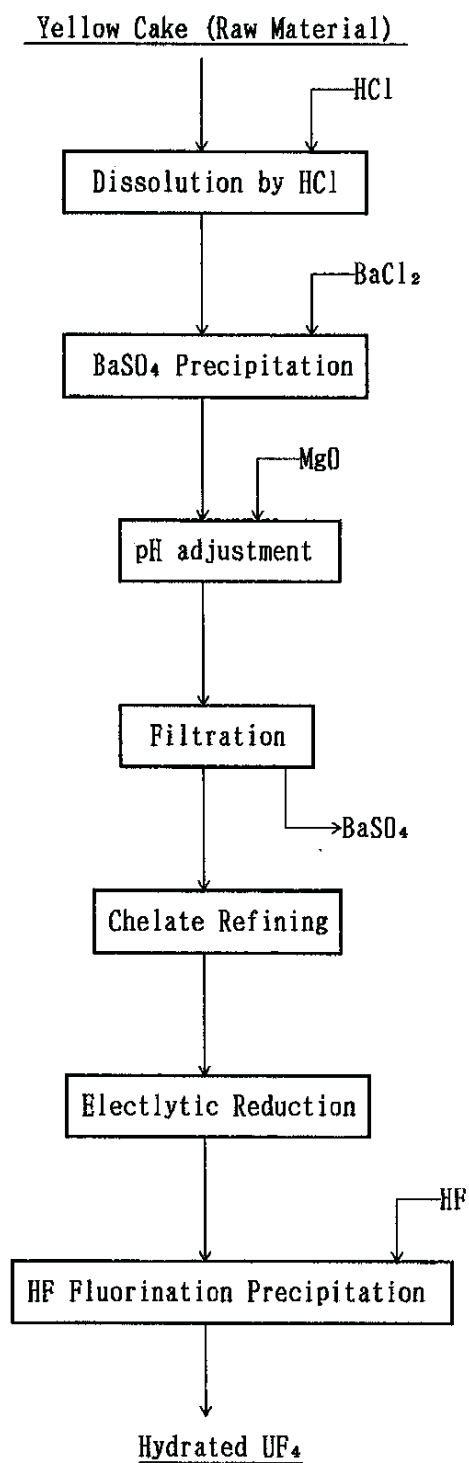


Fig. 2 The Block flow of the PNC method

Table 1

The list of the main equipments of
the chelate resin refining test facilities

N A M E	ITEM	SPECIFICATION
Cartridge Filter (F-209)	MODEL	vertical cylinder
	CAPACITY	0.04m ³
	MATERIAL	SS41/HRL
	SIZE	φ 300 × H550 (excluded corn)
	ELEMENT	10 μ — φ 65 × 500L
Chelate Refining Tower (T-201)	MODEL	vertical cylinder
	CAPACITY	3.0m ³
	MATERIAL	SS41/HRL
	SIZE	φ 1200 × H240 (excluded corn)
	RESINS	UR-50:1000 ℓ
MgO Vessel	MODEL	vertical cylinder
	CAPACITY	0.1m ³
	MATERIAL	PVC
	SIZE	448 × 448 × H610

Table 2

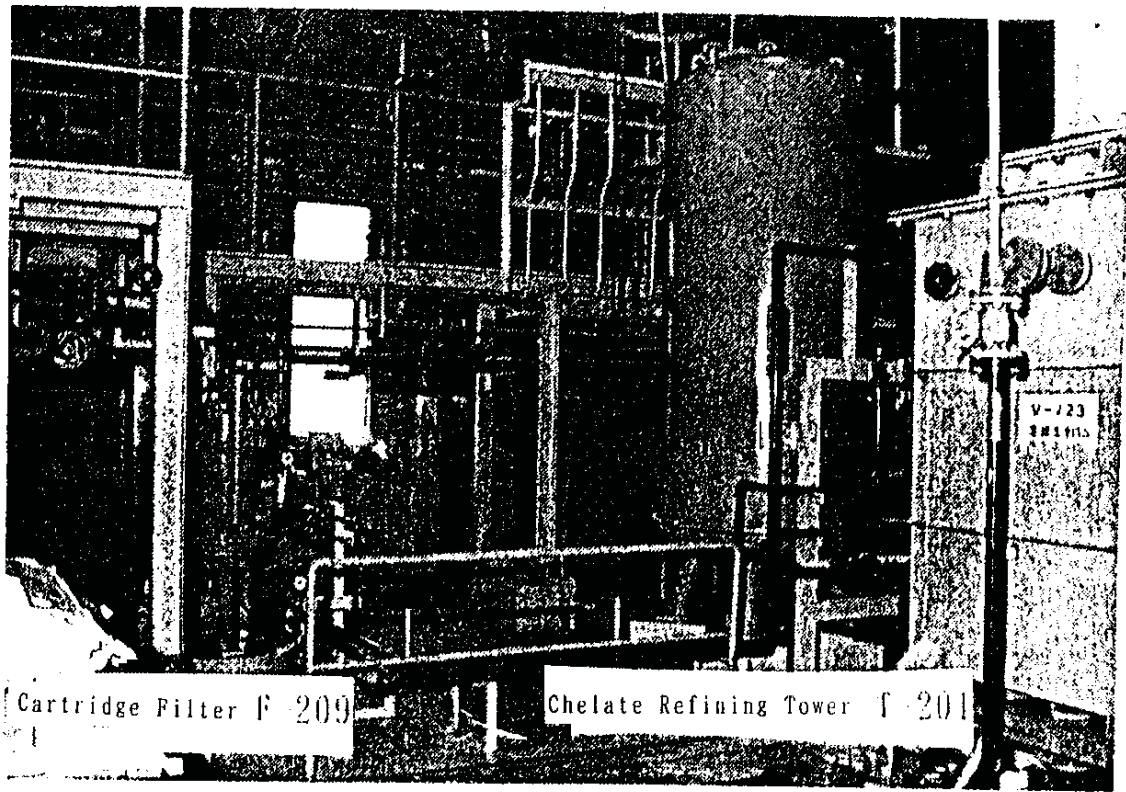
The behaviors of impurities on the chelate resin refining test run

element	Y.C. (ppm/U)	Filtrate of Y.C.Dessolving solution(ppm/U)	Chelate Resins Refining Sol. (ppm/U)	Chelate Refining D.F. (DF)
Ag	<3	<1	<1.3	—
Al	1510	1210	1310	1
Ba	341	19.7	21	1
Bi	<58	<9	<13	—
Ca	2410	3670	3910	1
Cd	<1.5	<0.5	<0.6	—
Co	<5	<5	<1.3	—
Cr	6.6	4.9	4.6	1
Cu	2.6	3.6	<2.6	6.8
Fe	3170	3620	535	360~ 500
K	2930	2440	2670	1
Li	<4	<2	<1.4	1
Mg	9550	24700	30100	1
Mn	308	283	276	1
Mo	1260	1630	62.6	26
Na	3410	15800	14200	1
Ni	3.5	3.9	3.8	1
Pb	11	11	12	1
Sb	<16	<2	<3	1
Sr	77.1	97.7	66.7	1
Ti	73	67	<13	> 5
V	737	737	331	2.2
Zn	25.7	29.6	31	1
U	67%	211g/ℓ	147g/ℓ	114g/ℓ

Table 3

The effect of chelate resin refining

element	Y.C. Dissolving solution (ppm/U)	Chelate Refining D.F. (DF)	Chelate Resins Refining Sol. (ppm/U)
Al	1200~1600	1	1300~1600
Ca	2000~3700	1	2200~3900
Cu	3.5~ 88	1.5~27	<3.5
Fe	1300~3600	3.5~ 7	360~ 500
K	1900~2500	1	2000~2700
Mo	1650	26	63
Na	8500~15800	1	9400~14200
Ti	70~ 330	> 1.5	<220
V	20~ 740	1~ 2.3	20~ 330



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Photograph

The chelate resin refining test facilities

BIBLIOGRAPHY

- 1) Yano, Tomoshige, Obara; Development of Chelate Resin Refining Technique
:PNC SJ4357 87-001
- 2) I.Yasuda et al.; The report on the research and development of the
milling and refining pilot plant :PNC ZN7410 88-006
- 3) Yunitika Ltd.; Chelate Resin for Adsorption of Heavy Metals

ACKNOWLEDGEMENT

We are pleased to acknowledge the considerable assistance of Dr.Hirono(Atomic Industries Co.,Ltd.) and are also grateful to Mr.Muranishi(UNITIKA Ltd.) for providing the very useful reports and brochures about Unicellex.

APPENDIX

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3 . UNITIKA Unicelllex"UR-20"	19
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6 . Procedure of Unicelllex"UR-50" in a laboratory	30

Structure of Unicellex

Unicellex manufactured by Unitika Ltd. is a iminodiacetic acid form resin which structure is phenol-formalin co-polymerization as shown below:

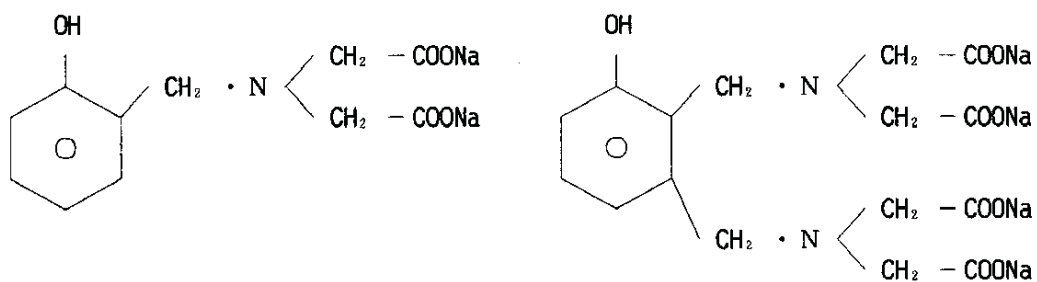


Fig. Structure on Chelate Form Group of Unicellex

UNITIKA UNICELLEX "UR-10"

1. Applications:

- 1) Reclamation of valuable metals like Zinc from waste water and its re-use for the plant.
- 2) Elimination of impure metals from the organic or inorganic substances.

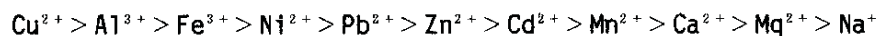
2. Form Supplied:

Loaded with sodium ions

3. Characteristics:

- a) "UR-10" has higher selectivity for regeneration is less than that required for conventional cation exchangers:

* Selectivity order:



- b) It is capable of refining metals and inorganic salts:

- c) Regeneration efficiency is high:

* The volume of eluent needed for regeneration is less than required for conventional cation exchange resin.

- d) It is reusable for long period:

4. Example of Application:

Reclamation of Zinc from waste water at PVA fiber plant:

Metal content in the water before treatment:

Zn: 10-25 (mg/ℓ)

Ca: 100-150 (mg/ℓ)

Metal content in the water after treatment:

Zn: less than 0.05 (mg/ℓ)

Ca: 100-160 (mg/ℓ)

Amount of water to be treated: 2400 (m³/Day)

Flow rate: 2.5 (gpm/ft³)

Zinc content in reclaimed ZnSO₄ solution: 8,000 (mg/ℓ)

Operating Facilities:

Sagoshi plant of Unitika Ltd.

2. Physical and Chemical Properties of "UR-10"

Appearance	Brown, Spherical
Form Supplied	Na ⁺ Form
Apparent Density	750 – 780g/ℓ (47 – 49 lb/ft ³)
Moisture Content	55 – 60%
Particle Size	20 – 50 mesh
Applicable pH	2 – 10
Applicable Temperature	70°C (158 ° F) MAX
Total Capacity	0.5 mol Cd ²⁺ /ℓ-resin (2.0 lb Cd ²⁺ /ft ³ -resin)
Flow Rate	3 – 30 ℓ/hr-ℓ-resin (0.4 – 4 gpm/ft ³ -resin)
Recommended Bed Depth	700 – 1500mm (30 – 60 inch)
Backwash Flow Rate	4 – 5 m/hr (1.6 – 2 gpm/ft ²)

UNITIKA UNICELLEX "UR-20"

1. Applications:

Treatment of waste water containing harmful heavy metals at Schools, Institutes, Plants.

2. Form Supplied:

Loaded with calcium ions

3. Characteristics:

a) Change of acidity of the water is negligible before and after treatment.e

* The pH values indicate 6.0 to 8.5 in the after treatment.

b) Exchange capacity is larger than that of the conventional chelating resins:

* For example, 0.6 mol Cu^{2+} / ℓ .R (2.4 lb/ft³)

c) Exchange rate between calcium and Metals are high:

d) The volume changes are negligible:

* In the stage of after treatment, resin volume is much the same as before treatment.

e) It can be used repeatedly:

4. Example of Application:

Treatment of waste water at a laboratory

Harmful metal content in the water after treatment:

Cd: 10 (mg/ℓ)

Amount of water to be treated: 20 (m³/Day)

Flow rate: 2.5 (gpm/ft³)

Cadmium content in the water after treatment:

Cd: less than 0.01 (mg/ℓ)

Operating Facilities:

Government Industrial Research Institute, Nagoya

2. Physical and Chemical Properties of "UR-20"

Appearance	Brown, Spherical
Form Supplied	Ca ⁺ Form
Apparent Density	800 – 850g/ℓ (50 – 53 lb/ft ³)
Moisture Content	37 – 42%
Particle Size	20 – 60 mesh
Applicable pH	3 – 10
Applicable Temperature	100 °C (212 ° F) MAX
Total Capacity	0.6 mol Zn ²⁺ /ℓ-resin (2.5 lb Zn ²⁺ /ft ³ -resin)
Flow Rate	3 – 30 ℓ/hr-ℓ-resin (0.4 – 4 gpm/ft ³ -resin)
Recommended Bed Depth	700 – 1500mm (30 – 60 inch)
Backwash Flow Rate	4 – 5 m/hr (1.6 – 2 gpm/ft ²)

UNITIKA UNICELLEX "UR-30"

1. Applications:

Reclamation of valuable metals like Nickel and copper from waste water and its re-use for the plant.

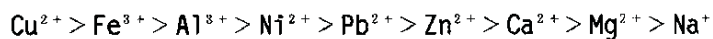
2. Form Supplied:

Loaded with hydrogen ions

3. Characteristics:

a) "UR-30" has higher selectivity to Nickel Copper etc., compared with conventional cation exchange resin:

* Selectivity order:



b) RTesin volume change is negligible before and after treatment.

c) Operation cost is economical:

* Operation cycle of Unicellex "UR-30" is:

"UR-30" — water treatment — Elution with acid — Renewed "UR-30"

d) It can be used repeatedly:

4. Example of Application:

Reclamation of Nickel from washing water in Nickel plating process:

Nickel content in the water before treatment:

Ni: 100 (mg/ℓ)

Nickel content in the water after treatment:

Ni: 0.1 (mg/ℓ)

Amount of water to be treated: 10 (m³/Day)

Flow rate: 2.5 (gpm/ft³)

Nickel content in reclaimed NiSO₄ solution: 2 – 5 %

Operating Facilities:

Brother Industry Ltd.

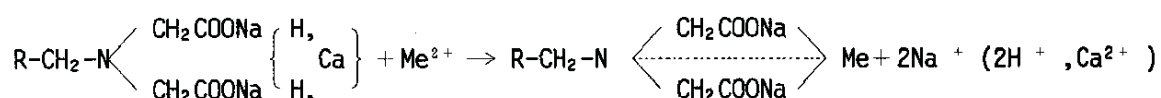
5. Physical and Chemical Properties of "UR-30"

Appearance	Brown, Spherical
Form Supplied	H ⁺ Form
Apparent Density	770 – 820g/ ℓ (48– 51 lb/ft ³)
Moisture Content	45– 50%
Particle Size	32– 70 mesh
Applicable pH	2 – 10
Applicable Temperature	100 °C (212 ° F) MAX
Total Capacity	0.8 mol Cu ²⁺ / ℓ -resin (3.2 lb Cu ²⁺ /ft ³ -resin)
Flow Rate	3 – 30 ℓ /hr-ℓ -resin (0.4– 4 gpm /ft ³ -resin)
Recommended Bed Depth	700 – 1500mm (30– 60 inch)
Backwash Flow Rate	4 – 5 m/hr (1.6 – 2 gpm/ft ²)

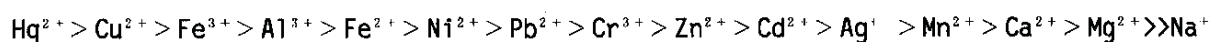
1. Introduction

Unicellex, a phenoric chelating resin, developed by Unitika Ltd., exhibits selective adsorption of the heavy metal ions such as lead, cadmium, nickel, zinc, etc.

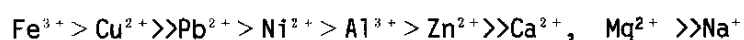
Supplied form of Unicellex "UR-10" is in sodium form, Unicellex "UR-20" is in calcium form, Unicellex "UR-30" is in hydrogen form, Unicellex "UR-40" is in sodium form, and Unicellex "UR-50" is in hydrogen form.



Unicellex "UR-10", Unicellex "UR-20", Unicellex "UR-30" and Unicellex "UR-40" have the following selectivity order for metal ion.



and Unicellex "UR-50" has the following selectivity order,



Utilizing this characteristic, it is possible to remove harmful metals or to reclaim valuable metals in the presence of multiple-metal-ion in a solution.

Characteristics of Unicellex

- 1) Making chelate with heavy metals, it is capable of removing them even in a solution containing many different cations such as Na^+ and Ca^{2+} , without being affected by such cations.
- 2) It removes heavy metal ions by making chelate with them even in a dilute aqueous solution, thus making the treatment more complete.
- 3) Utilizing outstanding selectivity for metal ions, it is possible to remove commercially a specific metal ion in the presence of multiple-metal-ion in a solution. For instance, Ca^{2+} and Zn^{2+} can be separated each other from a solution which dissolve both of them.

- 4) The metal saturated in the resin can be easily removed from the resin by applying a mineral acid and thereafter it can be used again. The volume of mineral acid solution needed for this elution is less than that required for elution of conventional strong cation exchange resins.
- 5) Production method of Unicellex is quite different from that of conventional chelating resins. A complex-forming group is introduced at the stage of monomer, and a patented process produces a perfect spherical resin directly.
- 6) Since the resin is spherical and very rigid, operation of a resin column is trouble-free and it can be used repeatedly without suffering damage from mineral acid and alkali.

Unicellex series consist of Unicellex "UR-10", Unicellex "UR-20", Unicellex "UR-30" , Unicellex "UR-40" and Unicellex "UR-50".

2. Physical and Chemical Properties of "UR-50"

Appearance	Brown, Spherical
Form Supplied	H ⁺ Form
Apparent Density	750 – 850g/ ℓ (49– 51 lb/ft ³)
Moisture Content	48– 58%
Particle Size	20– 60 mesh
Applicable pH	0.5 – 10
Applicable Temperature	100 °C (212 ° F) MAX
Total Capacity	0.5 mol Fe ³⁺ / ℓ -resin* (1.7 lb Fe ³⁺ /ft ³ -resin)*
Flow Rate	2 – 30 ℓ /hr-ℓ -resin (0.2– 4 gpm /ft ³ -resin)
Recommended Bed Depth	700 – 1500mm (30– 60 inch)
Backwash Flow Rate	5 – 10m/hr (2 – 4 gpm/ft ²)

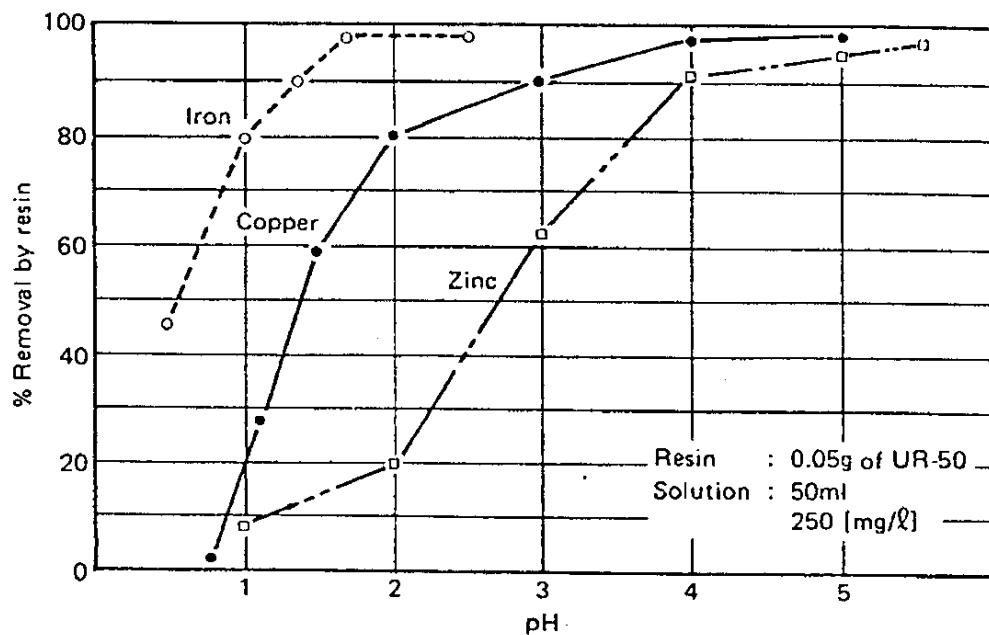
* at pH 2

3. Volume Change of Unicellex "UR-50"

Ionic Form	Resin Volume
H ⁺	1.00
Zn ²⁺	1.03
Ni ²⁺	1.04
Cu ²⁺	1.07
Fe ³⁺	1.10

4. Relationship between Chelating Ability and pH

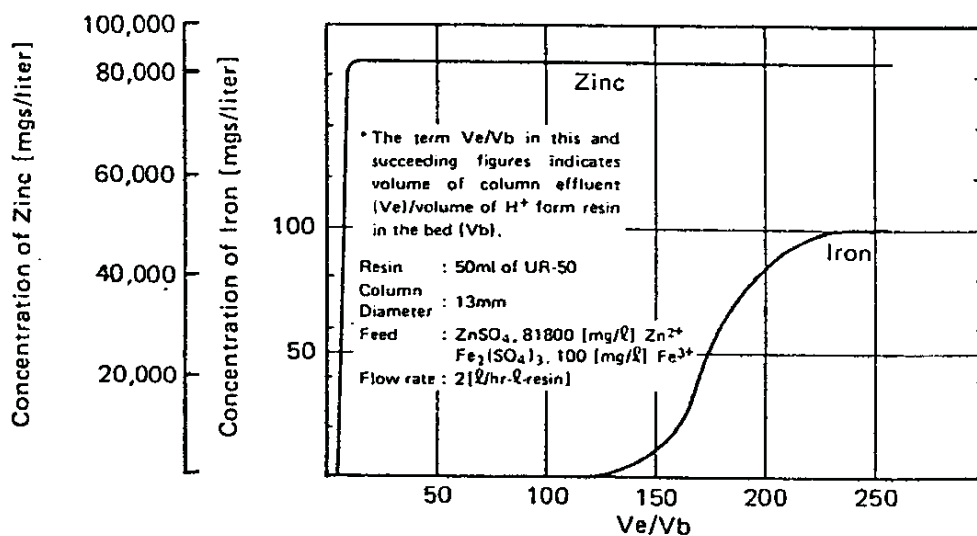
When a chelating resin makes a chelate with metal ions, the chelate forming ability is affected by pH of the solution. The figure below shows percentage of cation picked up by Unicellex "UR-50" (based on resin total capacity) at various pH levels.



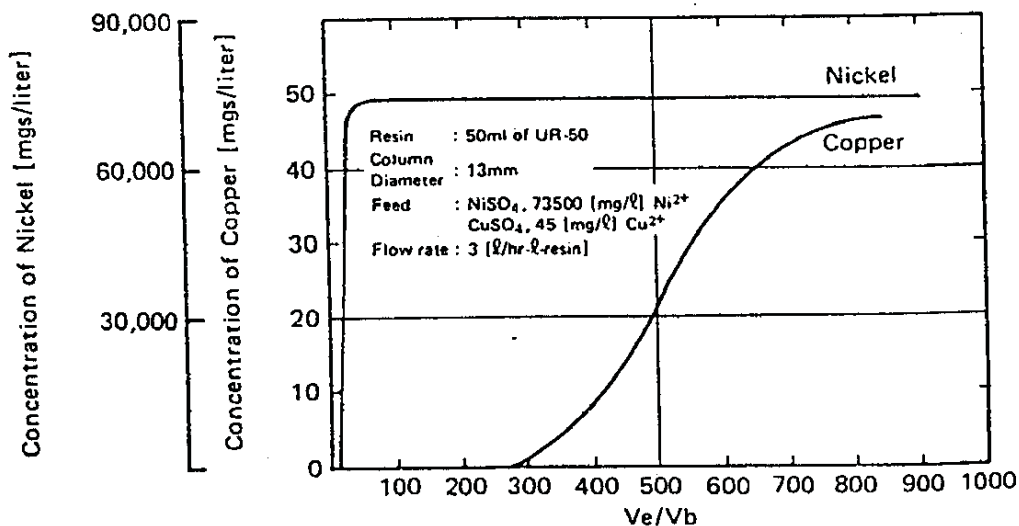
24 hours contact time

Percentage Cation Removal vs pH (in batch contact)

5. Examples of Break-through Curve



Break-through Curves for Iron in Zinc Solution



Break-through Curves for Copper in Nickel Solution

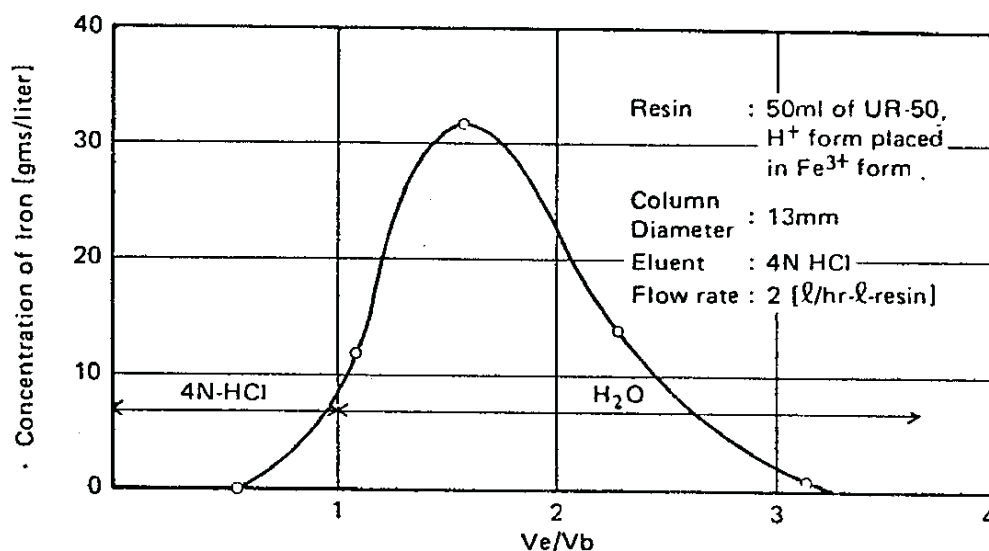
6. Elution of "UR-50"

"UR-50" saturated with metal ions is easily eluted by contacting it with either HCl or H_2SO_4 solution, the volume of which is about 1-2 times of the resin and after elution similar amount of fresh water is flown through the resin at flow rate of 1-2 (ℓ /hr- ℓ -resin).

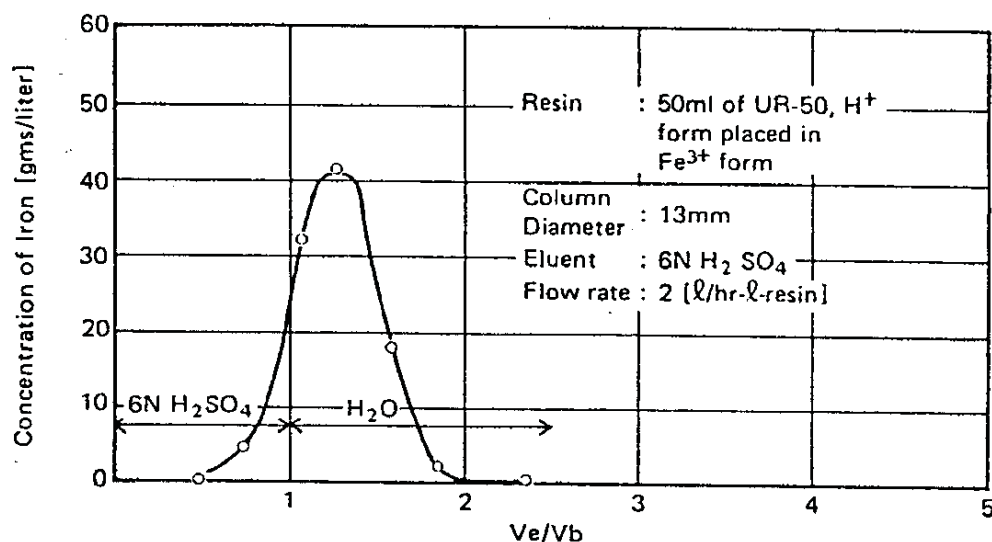
As a result of elution process, the resin is regenerated into H form.

Operation cycle of "UR-50" is:

H form resin - water treatment - elution with acid - regenerated "UR-50"

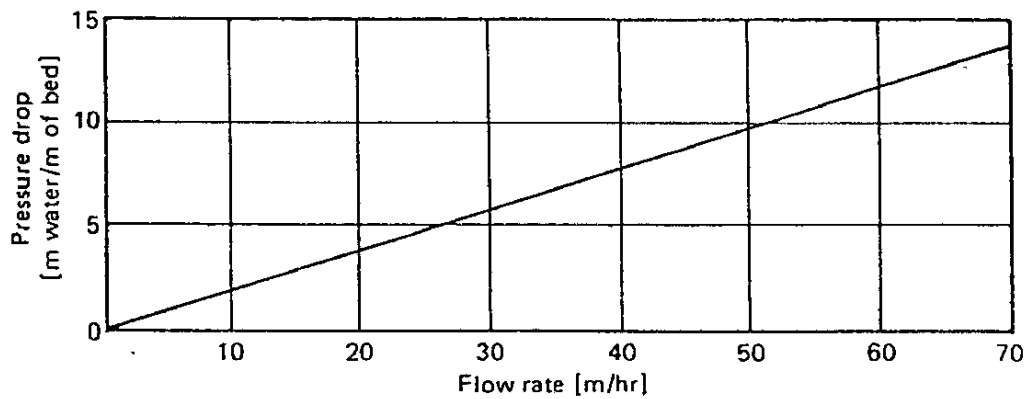


Elution of "UR-50" Saturated with Iron

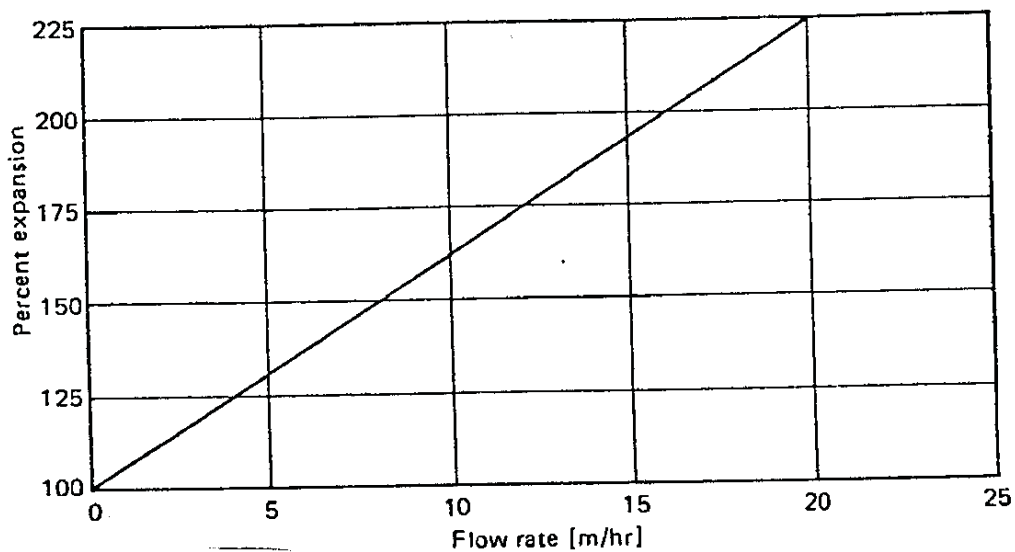


Elution of "UR-50" Saturated with Iron

7. Pressure Drop and Bed Expansion



Pressure Drop through "UR-50"



Bed Expansion of "UR-50"

8. Applications of Unicellex "UR-50"

- 1) Elimination of Iron from Zinc Sulfate plating bath.
- 2) Elimination of Copper from Nickel Sulfate plating bath.
- 3) Elimination of Iron from Aluminum Sulfate
- 4) Elimination of metal ion chelated with regand, such as Pyrophosphoric Acid, Amino Acid, ect.
- 5) Others.

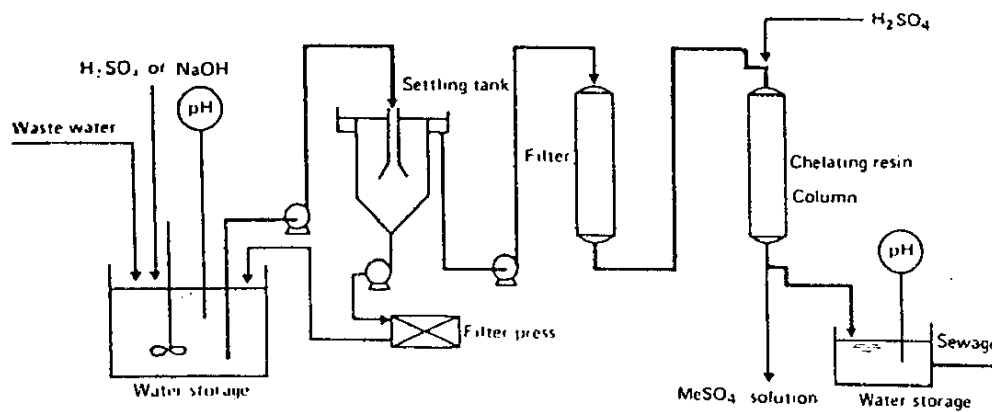
9. Operation Procedure

Unicellex resin is placed in a column at a height between 30-60 inches.

The effectiveness of metal adsorption depends primarily on contact time between the resin and the solution to be treated.

Therefore, it is important to feed the solution at a contact flow rate. Water treatment plant with Unicellex is similar to that with conventional ion exchange resins.

As shown in the example flow scheme, there are two ways to feed the solution into chelating resin bed, and either downflow or upflow is chosen depending on the conditions of the solution.



10. Supplement

Using Unicellex in water treatment, attention is requested to the following point:

1) Concentration of metal ions to be removed:

When a solution has highly concentrated metal ions to be removed, regeneration cycle of the resin becomes uncomfortably shorter.

In such case, it is advantageous to dilute the metal ion concentration beforehand by appropriate pre-treatment and then to proceed treatment by the resin afterward so that regeneration cycle becomes longer.

2) It is recommended to store the resin without opening shipping package.

Procedure of Unicellex "UR-50" in a laboratory

1. Form supplied:

Loaded with hydrogen ions

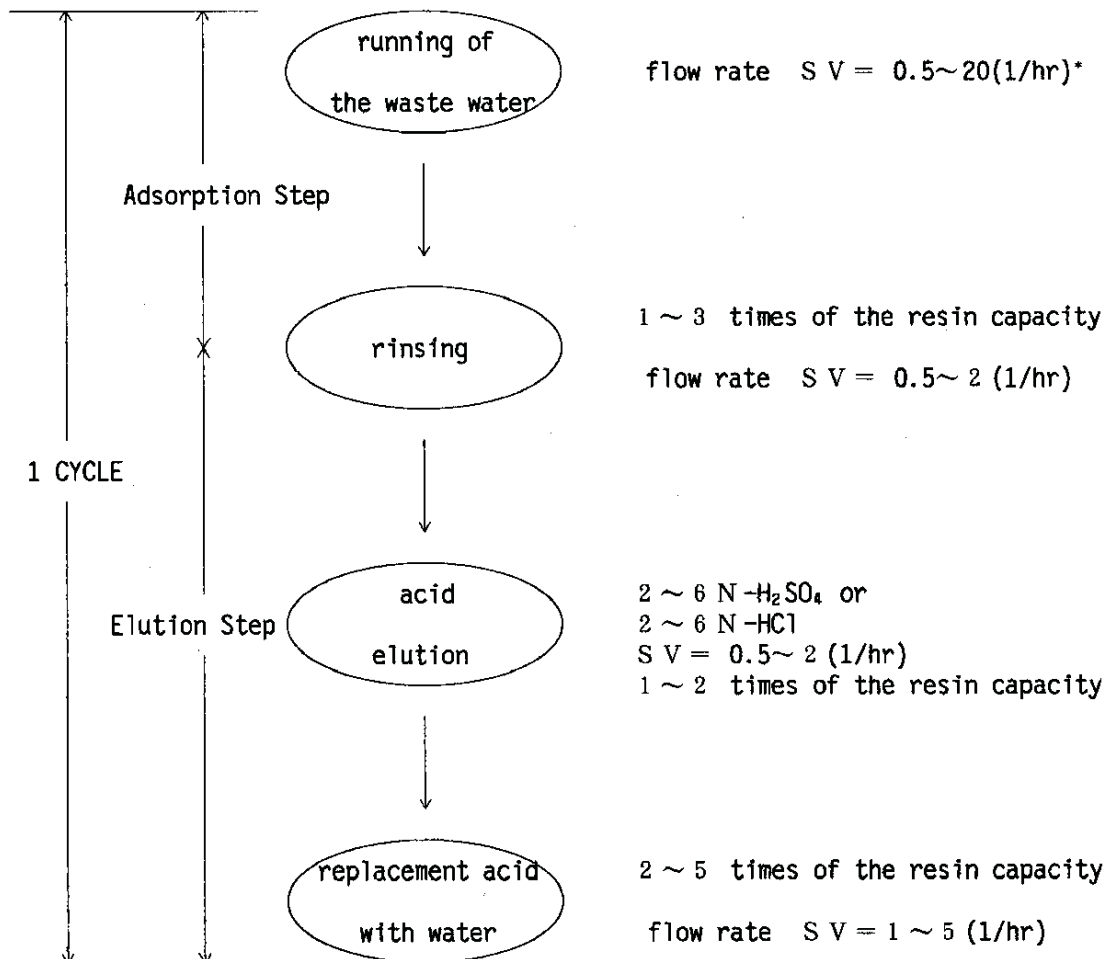
2. Preparation on the treatment of water

- 1) Soak "UR-50" in the ion exchange water sufficiently before using.
- 2) Pack "UR-50" with the ion exchange water in a column and the resin should be in the ion exchange water to prevent from generating the air bubble in the resin.

3. Adsorption and Elution

An adsorption step and an elution step in the laboratory are shown as below.

Keep more than 50cm of the resin height in the column.



* $SV=0.5 \sim 5$ is suitable for the elimination of iron or copper from high concentrated metal solution and $SV=5 \sim 20$ is suitable for the other cases.

COLOURIMETRIC DETERMINATION OF URANIUM

Date: 1982-12-17

Revision Date: 1985-09-03

Scope

This method is applicable for the *determination of* Uranium at the 5 to 100 ug U level in the sample aliquot, ~~the~~ relative standard deviation at the 100 ug U level is 4%.

Outline Of Method.

This is a modification of Johnson's and Florence's method. Uranium is oxidized to the +6 state with hydrogen peroxide and is then concentrated and removed from the major interfering elements by solvent extraction using TOPO/cyclohexane. A 1 mL aliquot of the extract is reacted with 0.05 % Bromo-PADAP/ethanol solution and the absorbance of the coloured complex is read by a spectrophotometer at 578 nm. The uranium content of the samples is calculated by regression analysis of the uranium standards absorption.

Apparatus

1. Bausch & Lomb Spectronic 710 spectrophotometer with the B & L micro flow-thru cell system or equivalent.
2. Shaker.
3. Vortex mixer.
4. 50 mL screw cap culture tubes.
5. 16 x 125 mm test tubes.
6. Dispensers.
7. Microliter pipettes.
8. Separatory funnels.
9. Eppendorf Repeater Pipette and Combitips 2.5 mL, 12.5 mL, 50 mL.

Reagents

1. Stock Complexing solution - suspend 25 g CDTA (Trans-1,2-Diaminocyclohexane-N N N' N'-tetraacetic acid), 65 g sulphosalicylic acid and 5 g sodium fluoride in 800 mL of deionized water, neutralize the solution with 40% sodium hydroxide until everything is in solution then adjust pH to 7.85 with 40% NaOH.
2. Dilute Complexing solution - dilute the Stock Complexing solution to 50% strength (by volume) with deionized water, then adjust the pH to 7.85 with 40% NaOH.
3. Buffer solution - dissolve 149 g of triethanolamine in 800 mL of water. Adjust the pH to 6.0 with 70% perchloric acid and allow to stand overnight. Readjust pH if necessary to 6.0 with perchloric acid then make up to 1 liter with deionized water.
4. 30% Hydrogen Peroxide
5. Anhydrous Ethanol (S.D.A.G.-1G 90% Ethanol/10% Methanol)
6. 5% Ascorbic acid - dissolve 25 g of ascorbic acid in 500 mL of deionized water.
7. Matrix adjustment solution - dissolve 20 g of sodium fluoride in 500 mL of deionized water, add 300 mL 85% orthophosphoric acid and dilute to 1 Liter with deionized water.
8. 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (BROMOPADAP) 0.05% in Ethanol - dissolve 1 g of BROMOPADAP in 2 L of anhydrous Ethanol.
9. 5 M Nitric acid - mix 1.25 L of 70% Nitric acid in 2.5 L of deionized water. Make to 4 litres.
10. 0.1 M Tri-n-octylphosphine oxide (TOPO) in cyclohexane - dissolve 154 g of TOPO in 4 L of cyclohexane.
11. Stock Uranium standard solution (1.0000 g/L U) - ignite black oxide standard at 850°C for 2 hours. Cool in desiccator, weight out correct amount to give 1.0000 g/L U and digest with 30 mL 70% nitric acid until solution is complete, then cool. Quantitatively transfer to a 100 mL volumetric flask and dilute to the mark with deionized water.
12. Working Uranium standard solution (100 ug/mL U) - pipet 10 mL the stock standard into a 100 mL volumetric flask. Add 5 mL 70% nitric acid then make to the mark with deionized water.

Procedure

1. Pipet aliquots of standards and samples containing 10 to 100 ug U into 50 mL culture tubes also run a blank.
2. Add 2 drops 30% hydrogen peroxide to the culture tubes.
3. Add 2 mL of matrix adjustment solution to the standards and blank only.
4. Dispense 10 mL of 5 M nitric acid into each culture tube.
5. Add 2 mL of 5% Ascorbic acid to each culture tube.
6. Adjust the volume in each culture tube to 25 mL with deionized water.
7. Dispense 3.0 mL of 0.1 M TOPO solution into each culture tube then cap with the screw caps. Shake all the tubes on the mechanical shaker for 4 minutes.
8. Allow the phases to separate. Pipet 1 mL of the organic phase into a clean 16 x 125 mm disposable glass test tube.
9. Pipet 0.5 mL of dilute complexing solution into the test tube and mix.
10. Dispense 2.0 mL of 0.05 % BROMOPADAP solution into the test tube and mix.
11. Pipet 0.5 mL of buffer solution into the test tube and mix.
12. Allow to stand for 5 minutes for colour development. Then dispense 4.0 mL of anhydrous alcohol into the test tube and mix until there is a homogeneous solution.
13. Set the spectrometer wavelength to 578 nm. Set 0 absorbance with the blank and read the absorbance of all the sample and standards. (Refer to the manufacturer's suggested operation procedure for operating the spectrometer)
14. Perform a Beer's Law plot either graphically or mathematically and calculate the concentration of uranium in the sample.

ORGANIC SAMPLE PREPARATION FOR COLOURIMETRIC URANIUM ANALYSIS

Reagent

Stripping Solution - Dissolve 20 g of ferrous sulphate in 500 mL of deionized water, add 400 mL of 85% orthophosphoric acid, add 30 mL of 48% hydrofluoric acid. Dilute to 1 L with deionized water.

Store in a plastic bottle.

Procedure

1. Pipet 10 mL of stripping solution into a 125 mL teflon separatory funnel.
2. Pipet 10 mL of organic solution containing 5 - 300 ug/mL U into the separatory funnel.
3. Cap and shake vigorously for 3 minutes.
4. Allow the phases to separate. Pipet an appropriate amount of the aqueous phase into the 50 mL screw cap culture tube and proceed with the colourimetric uranium analysis.

本資料はセンターで浮遊選鉱試験を実施するにあたりPNC が説明用として作成した浮遊選鉱試験手順書及びデータシートである。

Procedure of the experiment of flotation

1. Preparation

- (1) weigh a certain quantity of the ground ore
- (2) weigh a certain quantity of water
- (3) put a certain volume of promoter in 10 ml measuring cylinder and bring the volume to 10 ml with water
- (4) set up the vessel and the flotation machine and add the ore and water
- (5) mix the ore and water uniformly
- (6) measure the pH value and temperature of the pulp without bubbling
- (7) adjust the pH value by addition of HCl/NaOH solution

2. Test

- (1) adjust the revolution ratio and stir
- (2) add a certain volume of diluted promoter and bubble with a certain volume air in a vessel
- (3) scrape the generating babbles completely by a scraper and correct the scraped bubbles in a vat

3. After-treatment

- (1) stop the flotation machine and measure the pH value and temperature of the pulp
- (2) dispose the pulp by the suitable way and clean up the flotation machine and so on

4. Analysis

- (1) filter the bubbles through a filter paper and rinse the concentrate by spraying pure water on it
- (2) dry the concentrate thoroughly and weigh it
- (3) analyze the concentrate by chemical method

DETA SHEET OF FLOTATION EXPERIMENT (A)

[illegible]

DETA SHEET OF FLOTATION EXPERIMENT (B)

No	I T E M S	T I M E (min)				
		0 ~ 1	1 ~ 2	2 ~ 4	4 ~ 8	8 ~ 12
1	composition of froth <div> { solid in froth (g) liquid in froth (g) </div> ore content in floth (wt%)					
2	composition of froth <div> { solid in froth (g) liquid in froth (g) </div> ore content in floth (wt%)					
3	composition of froth <div> { solid in froth (g) liquid in froth (g) </div> ore content in floth (wt%)					
4	composition of froth <div> { solid in froth (g) liquid in froth (g) </div> ore content in floth (wt%)					
3	composition of froth <div> { solid in froth (g) liquid in froth (g) </div> ore content in floth (wt%)					
4	composition of froth <div> { solid in froth (g) liquid in froth (g) </div> ore content in floth (wt%)					

本研究交流に当たり、以下の選鉱用試薬をPNC より持参した。

試薬の種類	商 品 名	化学的構造	類 似 品
気泡剤			
1. バイン油	NKY Pine oil No.10	テレピン アルコール	Yarmor F. Flotol B
2. アルコール	NKY frother No.623	C ₅ - C ₁₀	Aerofroth 71A Montanol 300
3. クレゾール酸	NKY frother No.18 NKY frother No.183	クレゾール + バイン油 クレゾール + タール	
4. グリコール	NKY frother No.400 Aerofroth 65	グリコールエーテル	Aerofroth 65 Dowfroth 250
捕集剤			
1. 硫化鉱物用	NKY promoter SN-B NKY promoter 120-T NKY promoter 260	メルカプトベンゾチアゾール	Aero 404
2. 非硫化鉱物用	NKY promoter DT NKY promoter DT-A NKY promoter SP-S Aero 825 Aero 840 Aero 830 Aero 845 NKY promoter F-2	 オレイン酸	Duomeen T Duomac T Aero 825 NKY promoter SP-S NKY promoter SP-S Aero 723
抑制剤	NKY D-QC Aero depressant 633	タンニン酸	Quebracho

FACSIMILE MESSAGE

FM No.

038/11

Date Nov 6, 1991

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TO: Name

Ippei Amamoto

FROM: Name

Y M Song

Location Power Reactor & Nuclear Fuel
Dev Corp

Location CY SIN

CC: Fax #81-33-5051552

RE: CYANAMID MINING CHEMICALS AND FLOCCULANTS

I was informed by K N Chen that you are working on a project in Indonesia and are in need of some mining chemicals and flocculants.

Please kindly provide details (specifications, quantity and required date, etc. to me at:

Cyanamid (Far East) Limited
190 Middle Road
#09-04/05 Fortune Centre
Singapore 0718

Tel : 337-0222

Fax : 337-3391

Regards

Y M Song
Director-Chemicals

OFFICE OF THE REPRESENTATIVE
mitsui-cyanamid, ltd. - SINGAPORE

65, CHULIA STREET #38-04 OCBG CENTRE,
SINGAPORE 0104 TEL NO: 534-2611
FAX: (65) 535-5161

FACSIMILE MESSAGE No: 07/11

To: MR IPPEI AMAMOTO	Page: 1 of 1
Company/Location: NINGYO TOGE WORKS - OKAYAMA PREF	Date: 12 NOV 1991
From: K N CHEN	C.C.: MR Y YASUDA - MCY

THANKS YOUR FAX. ^{OF NOV. 82} PLEASE PROCEED TO WORK WITH MR SONG OF CFE FOR CYANAMID'S MINING CHEM WHEN YOUR ANALYSIS DATA ARE AVAILABLE.

AS FOR FLOCCULANTS, WE NEED MORE INFO BEFORE RECOMMENDING ACCOFLOC GRADES. INFO SUCH AS PH, SS(%), TYPE OF CLAY, FEED FLOW RATE, TYPE OF THICKENER (& DIMENSIONS) ETC. ARE NECESSARY INFO. ~~TAKE~~ TAKE YOUR TIME TO LOCATE THESE INFO AND WE DISCUSS FURTHER ONCE AVAILABLE.

FOR YOUR REF OUR ACCOFLOC A125 PERFORMS VERY WELL IN MAMUT COPPER MINE UNDER MOST CONDITIONS BUT SOME SPECIAL ORES WOULD VERY MUCH AFFECT FLOCCULANT PERFORMANCE. PLANT HYDRAULICS ARE ALSO IMPORTANT - IF SHEARING TOO STRONG, FLOCCULANT PERFORMANCE POOR. SOME ADJUSTMENTS IN DOSING POINTS WOULD IMPROVE OPERATION.

UNTIL WE MEET OR DISCUSS AGAIN, BEST REGARDS TO YOUR FAMILY AND COLLEAGUES.