



# Bergvesenet

Postboks 3021, N-7441 Trondheim

## Rapportarkivet

|                                       |                    |                           |                      |                     |
|---------------------------------------|--------------------|---------------------------|----------------------|---------------------|
| Bergvesenet rapport nr<br><b>5709</b> | Intern Journal nr  | Internt arkiv nr          | Rapport lokalisering | Gradering           |
| Kommer fra ..arkiv<br>AS Megon        | Ekstern rapport nr | Oversendt fra<br>Elkem AS | Fortrolig pga        | Fortrolig fra dato: |

### Tittel

Rapport fra studiereise i England og USA 27.20 - 13.11.1970 og påfølgende diskusjoner i Norge vedr. oppredning Fen, salg av  $Y_2O_3$ , patentspørsmål og kjøp av xenotim

### Forfatter

Odd Eidsmo

Dato    År

2.12 1970

### Bedrift (oppdragsgiver og/eller oppdragstaker)

AS Megom

|                 |                   |              |                             |                              |
|-----------------|-------------------|--------------|-----------------------------|------------------------------|
| Kommune<br>Nome | Fylke<br>Telemark | Bergdistrikt | 1: 50 000 kartblad<br>17134 | 1: 250 000 kartblad<br>Skien |
|-----------------|-------------------|--------------|-----------------------------|------------------------------|

### Fagområde

Oppredning

### Dokument type

### Forekomster (forekomst, gruvefelt, undersøkelsesfelt)

Fensfeltet

### Råstoffgruppe

Industrimineral

### Råstofftype

RE

### Sammendrag, innholdsfortegnelse eller innholdsbeskrivelse

Rapporten inneholder korespondanse med og referat fra møter/besøk i forbindelse og forsøk på å opprette kontakt med firmaer i USA som kunne utføre oppredningsforsøk på Fensmalmen.

Ans.

RAPPORT FRA STUDIEREISE I ENGLAND OG USA, 27.10. - 13.11.70  
OG PÅFØLGENDE DISKUSJONER I NORGE VEDR. OPPREDNING FEN,  
SALG AV  $Y_2O_3$ , PATENTSPØRSMÅL OG KJØP AV XENOTIM

INNHold:

1. Rapport fra besøk ved Warren Spring Laboratory 27.10.70, ved Gunnar Thorsen.
2. Brev fra Warren Spring Laboratory, datert 29.10.70.
3. Reiserapport fra besøk ved Sylvania Electric Products Inc., Towanda, samt notater fra møter i New York angående patent-spørsmål og råstoffer, ved Orvar Braaten og Bjørn Gaudernack.
4. Rapport fra studiereise i USA, ved berging. Odd Eidsmo.
5. Brev fra American Cyanamid Company, datert 16.11.70.
6. Brev fra Colorado School of Mines Research Institute, datert 13.11.70.
7. Brev fra The Galigher Company, datert 13.11.70.
8. Besøk ved U.S. Bureau of Mines Research Station, Reno, Nevada, 11.11.70, ved O. Braaten.
9. Rapport fra dr. Smidts besøk i Norge i tiden 22.-27.11.70 ved cand. real. P. Chr. Sæbø.
10. Brev fra Hazen Research, Inc., datert 4.12.70.

+ Reiserapport fra O. Eidsmo og div. annet.

OB/kk

10.12.70

Dosent Gunnar Thorsen,  
Institutt for kjemiteknikk, NTH,  
p.t. University of Bradford.

RAPPORT FRA BESØK VED WARREN SPRING LABORATORY 27.10.1970

Til stede: Mr. L.D. Muller, Mineralogy Section,  
Mr. D.V. Jackson, Metals Extraction Division,  
Mr. T.J. Hickey, Mineral Processing Division,  
Overing. O. Braaten, A/S MESCON,  
Dosent G. Thorsen, Institutt for kjemiteknikk, NTH.

Hensikten med besøket var å diskutere hvilke muligheter som foreligger for oppgradering og utnyttelse av malmen fra Fensfeltet. Med Warren Springs erfaring og ekspertise, spesielt fra arbeider med malmer fra Mima Hill og Kangankunde, bør deres vurdering veie tungt for de videre disposisjoner.

Det fremgikk av samtalen at man anså opparbeidelsen av malmen fra Fensfeltet som meget vanskelig. Det var blitt knyttet visse forhåpninger til en kalsineringsmetode for behandling av karbonatene hvorved kalsiumoksyd vaskes ut med vann og de sjeldne jordarter oppkonstreres i residuet. Dette var med hell blitt utført med malmen fra Kangankunde hvor de sjeldne jordarter forelå som monazit. Warren Spring Laboratory hadde foretatt noen orienterende undersøkelser med denne metoden med prøver fra Fensfeltet, men med negativt resultat. Dette skyldtes for det første at jerninnholdet i den ankeritholdige dolomit gjorde utvaskingen vanskelig, og dessuten har det vist seg at jordartene foreligger vesentlig som fluorkarbonater som nedbrytes ved kalsineringen på like linje med de øvrige karbonater.

*Kan også skyldes at RE-mineralene opptrer bundet i karbonatene.*

Mr. Muller hadde foretatt visse mikrosondeundersøkelser av de tilsendte prøver og nevnte spesielt at det var påvist cerium, lantan og dysprosium.

Braaten gjorde rede for de forskjellige områder innenfor Fensfeltet, og feltets heterogene karakter ble fremhevet. Fra Warren Springs side ble det hevdet i denne forbindelse at de forskjellige områder måtte betraktes og håndteres hver for seg. Det ble fremholdt meget bestemt at man ikke kunne regne med at den metode som eventuelt ble utviklet for behandling av malmen innenfor ett område, kunne overføres til de øvrige områder innenfor feltet.

Det generelle inntrykk fra samtalen var at Warren Spring Laboratory ga en

meget nøktern og gjennomtenkt vurdering som i hovedsak gikk ut på at forut for konkrete oppredningsforsøk er det nødvendig med omfattende kvalitative og kvantitative mineralogiske undersøkelser. Det ble dessuten påpekt at mineralogiske undersøkelser som utføres med sikte på kommersiell utnyttelse av malmen, bør gjøres i intim kontakt med neste ledd i prosessen, dvs. oppgraderingssiden.

Da mineralogiske undersøkelser er både tidkrevende og kostbare, ble det anbefalt at man i første omgang konsentrerer undersøkelsene om det område innenfor Fensfeltet som blir ansett som mest lovende ut fra en totalvurdering av sammensetningen.

På grunn av forsinkelser ved flyavgangen fra Oslo, måtte møtet utsettes i forhold til den opprinnelige plan. Dette medførte at Mr. A.W. Fletcher, Head of Metals Extraction Division, ikke hadde anledning til å være tilstede. Under en samtale som undertegnede hadde med Mr. Fletcher to dager senere, ble det imidlertid fra Mr. Fletcher's side fremholdt at det burde være vel verdt å foreta en nærmere utredning og undersøkelse av alternative prosessganger basert på kjemiske<sup>og</sup> pyrometallurgiske metoder. Mr. Fletcher vil gjøre nærmere rede for dette i sitt brev til A/S MEGON.

Det synes i denne forbindelse å være grunn til å peke på at Mr. Fletcher hører til de fremste eksperter innenfor ekstraktiv metallurgi. Selv om de nye veier som blir antydnet ikke skulle være teknisk/økonomisk anvendelige, vil undersøkelsene kunne gi impulser og rom for nytenkning som kan være av uvurderlig betydning for fremtidig aktivitet på andre områder, eksempelvis med tanke på alternative prosessganger for de mer konvensjonelle metaller.

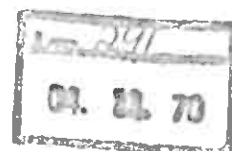
Av samtalene fikk man inntrykk av at Warren Spring Laboratory anser forekomstene i Fensfeltet som meget verdifulle. Ved undertegnades tidligere besøk den 1.10.70 ble det således uttalt at dersom man hadde hatt tilsvarende forekomster i Storbritannia, ville dette ha vakt betydelig interesse på britisk industrihold med stor konkurranse om rettighetene.

Bradford, 9. november 1970

*Gunnar Thorsen*  
Gunnar Thorsen



DEPARTMENT OF TRADE AND INDUSTRY  
Ministry of Technology  
WARREN SPRING LABORATORY  
Gunnels Wood Road, STEVENAGE, Hertfordshire  
Telex: 82250 Telephone: Stevenage 3388



Please address any reply to  
THE DIRECTOR

and quote: 25/3/65  
Your reference: OB/KK

29 October 1970



*Carverton 1/10*

Dr Orvar Braaten  
Project Manager  
MEGON  
Elkemhuset  
PO Box 5130  
Oslo 3  
NORWAY

Dear Dr Braaten

I was sorry that your plane was delayed and I was unable to meet you when you visited this Laboratory on 27 October. However, I understand that you had a useful discussion with Messrs Muller, Hickey and Jackson.

Processing the Ben carbonatite is an extremely complex problem. Following the discussions we would suggest the following approach:

- 1 Selection of an area of the deposit for detailed study. The selection should be based on adequate reserves of essentially one ore type containing recoverable values in addition to the rare earths. Present evidence suggests that apatite is the most likely additional value although pyrochlore may be worth considering. It is possible that you may already have made this selection in deciding to concentrate on the intermediate zone described in the discussions.
- 2 Preparation of a suitable sample or samples that can be considered reasonably representative of the reserves in the area selected.
- 3 Detailed applied mineralogical investigations on the samples to identify and quantify the minerals present, the distribution of values, particularly rare earths and europium in these minerals and determination of the liberation size of the important minerals.

It is considered inadvisable to start any beneficiation studies until the mineralogical studies are complete. The calcination process that has been discussed with you appears inapplicable for two reasons, firstly the iron content of the dolomite/ankerite prohibits satisfactory slaking of the calcined product and secondly because the rare earths appear to be present as fluorocarbonates and not monazite and the fluorocarbonates will decompose during calcination.

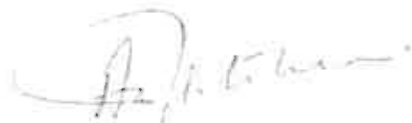
Chemical extraction processes are unlikely to be economically viable without preconcentration of the rare earths and this is dependent on the mineralogical findings. However, it is possible that Dr Thorsen might like to carry out preliminary feasibility studies of routes which we could suggest such as salt roasting, alkali fusion and other heat treatments followed by leaching while he is in this country. Such routes

/will have.....

will have to be considered if it is established that the rare earth minerals are in the 1 to 2 micron particle size range.

If you wish us to do the necessary mineralogical work and any subsequent beneficiation studies we shall be pleased to assist. In this event, a timed and costed project proposal would be submitted for your approval and probably a further meeting to discuss samples would be desirable. A request for work along these lines would be best addressed to Mr A S Joy who is Head of our Mineral Processing Division.

Yours sincerely

A handwritten signature in dark ink, appearing to read 'A. W. Fletcher', with a stylized flourish at the end.

(A W FLETCHER)

Head, Metals Extraction Division.

## REISERAPPORT

fra besøk ved Sylvania Electric Products Inc., Towanda, samt notater fra møter i New York angående patentspørsmål og råstoffer.

Ved Orvar Braaten og Bjørn Gaudernack.

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1. BESØK VED SYLVANIA ELECTRIC PRODUCTS INC., TOWANDA
2. - 3. NOV. 1970

### 1.1. Generelt om Sylvania og forholdet Megon/Sylvania

I Towanda, Pennsylvania, har Sylvania Electric Products Inc. (Subsidiary of General Telephone & Electronics) sin Chemical and Metallurgical Division. Her produseres fosforer for TV og belysning, wolfram-, molybden- og germaniumprodukter, hullmasker for TV-apparater, samt diverse andre kjemiske og metallurgiske produkter. Virksomheten ble etablert i 1941, og avdelingen har nå ca. 1400 ansatte. Nærmere beskrivelse av firmaet er gitt i følgende trykksaker, som er vedlagt originalen til denne rapport:

1. "Innovators in Chemistry and Metallurgy", Sylvania Electric Products Inc./Chemical and Metallurgical Division/Towanda, Pennsylvania.
2. "Sylvania in Towanda", 25th Anniversary, 1941 - 1966.

O. Braaten og B. Gaudernack ankom til Towanda om formiddagen den 2. november, og møtte i løpet av dagen følgende representanter for Sylvania:

Dr. Richard W. Mooney, vice president & general manager,  
Mr. C.H. Sparrow, manager, contracts and market services,  
Mr. Walther S. Eberhard, manager of materials,  
Mr. Leon F. Dennis, manager of engineering,  
Dr. Felix F. Mikus, manager of phosphor research,  
Mr. James E. Mathers, engineer, phosphor research,

Vi hadde 3 uker før besøket sendt en prøve på ca. 100 g  $Y_2O_3$  (produsert ved Adogen-ekstraksjon i IFA's laboratorium) til Sylvania for analyse

og testing. Disse undersøkelser var fullført bortsett fra analysen på Ce, som ble ferdig 3. november. Av analyserapportene, som følger som bilag, fremgår det at det ble påvist 4 ppm Ce, 1,3 ppm Dy og 1 ppm Tm. De øvrige SJ-elementer var under påvisningsgrensene. Mengdene av andre forurensninger var også meget små, ifølge den kvalitative spektrografiske analyse.

Folkene i "Phosphor Research" (Mikus, Mathers) sa at denne prøven representerte det reneste  $Y_2O_3$  de noen gang har hatt til undersøkelse. Videre erklærte de seg meget interesserte i et slikt superrent  $Y_2O_3$  ("we have been looking for this kind of material for years!"). Riktignok hadde en foreløpig fosfortest med den tilsendte prøven ikke falt helt tilfredsstillende ut, idet tilstrekkelig "brightness" ikke ble oppnådd. Det kunne ikke umiddelbart gis noen forklaring på dette, men det ble antydnet at man kanskje kunne få bedre resultat ved å "dope" produktet, dvs. tilsette kontrollerte ppm-mengder av andre SJ. I alle fall ble det understreket at man ikke på grunnlag av denne ene testen behøvde å slutte at vårt produkt ikke kan brukes for fosforfremstilling. De sa videre at dersom vår prøve er representativ for et produkt vi kan levere, vil en slik kvalitet kunne åpne helt nye perspektiver for anvendelser av  $Y_2O_3$ .

Den prøven vi hadde sendt, var brukt opp og de ba om mer av samme slaget, heldigvis hadde vi med ytterligere 100 - 150 g, som vi ga dem. De trengte dessuten en større prøve for videregående tekniske undersøkelser (production test), og vi lovet at vi snarest mulig skulle fremstille 3 - 4 lbs av samme kvalitet og sende det til Sylvania innen årets utgang. Vi vil så sammen med Sylvania prøve å komme frem til et program for produksjon av større mengder i pilot-anlegget. Vi antydnet at vi kunne være "on stream" med Adogen-prosessen i februar 1971 og deretter øke produksjonen gradvis, kanskje til en samlet produksjon på 2 - 3000 kg i løpet av 1971. Klarer vi fortsatt å holde kvaliteten, vil vi sannsynligvis stå meget sterkt konkurransemessig sett og være sikret avsetning for alt vi kan produsere i pilotanlegget, forutsatt at vi kan holde en konkurransedyktig pris.

Prisspørsmålet ble forøvrig ikke drøftet i noen særlig utstrekning, men det falt selvsagt en del bemerkninger i det området, således at dagens pris på phosphor grade  $Y_2O_3$  ligger på:

US \$ 27 pr. lb, dvs. kr. 425 pr. kg.

Vi erklærte at vi var villige til å levere og trodde oss i stand til å produsere  $Y_2O_3$  til markedets laveste pris.

Vi antydte også muligheten av eksklusivitet overfor Sylvania, men de understreket sterkt at vi skulle stå fullstendig fritt til å selge til hvem vi vil (likesom Sylvania selvsagt må stå fritt i sine innkjøp av  $Y_2O_3$ ). Sylvania (Cal Sparrow) vil sende Megon et brev, som gir deres konklusjoner på våre samtaler og anbefalinger for hvordan vi bør gå frem i neste fase.

Richard Mooney karakteriserte markedet for  $Y_2O_3$  som "volatile". For tiden er etterspørselen liten, men plutselig kan det melde seg et behov for f. eks. 5000 lbs som må skaffes i løpet av noen uker. Produzentene må derfor være villige til å bære risikoen ved å sitte med forholdsvis store lagre av ferdig produkt. Situasjonen idag er da også at alle de større produsentene sitter med lagre av både råvarer og ferdig produkt. Ifølge Cal Sparrow må det bli en "shake-out" på dette markedet i løpet av 1971.

Leon Dennis nevnte at Sylvania driver med forskning og utvikling av keramiske materialer, og at de her har funnet en potensiell anvendelse for  $Y_2O_3$  av lavere renhetsgrad. Han mente at det vil kunne bli et betydelig marked for slikt  $Y_2O_3$  innen keramisk industri, dersom prisen blir lav nok (\$ 5 - 10 pr. lb). I løpet av våre samtaler kom det også frem at Sylvania er interessert i scandium (anvendes i lampefosforer) og i rhenium, som de bruker i produksjonen av W-Rh glødetråd. Markedsutsiktene for disse metaller ble betegnet som gode.

## 1.2. Omvisning i laboratoriene

Vi ble vist rundt i forsøks- og analyselaboratoriene til "Phosphor Research" gruppen av James Mathers, ledsaget av Cal Sparrow og (delvis Dr. Mikus. Eksperimentell forfremstilling foregikk i laboratorier dominert av glødeovner, for det meste mostandsovner for temperaturer opp til ca.  $1500^{\circ}C$ , men også induksjonsovnene for høyere temperaturer. De fleste ovnene er utstyrt for gløding under spesielle atmosfærer, som er nødvendig ved fremstilling av fosforer på sulfidbasis.

Vi så også laboratoriene for testing av fosforer. Prepareringen av "slides" for fluorescensmålinger foregår omtrent som følger: Finmalt fosfor suspenderes i en kaliumsilikatløsning ved rysting i en Erlenmeyer, deretter fordeles suspensjonen gjennom en dyse i et større volum av en fortynnet acetat-løsning. Faststoffet sedimenterer og danner et tynt belegg på prøveplaten, en kvadratisk glassplate ca. 4 x 4 cm (0,2 - 0,3 g fosfor pr. plate). Etter tørking blir fire slike "slides" montert på en sirkulær glasskive, tre prøver samt en standard for sammenligning. Prøveoppsatsen plasseres i et demonterbart katoderør som så lukkes og evakueres før testingen. En del av lyset som emitteres av fosforet ved elektronbestrålingen, ledes gjennom en Lucite-stav, omviklet med lystett tape, til analysatoren. Dette er et Czerny-Turner Scanning Spectrometer fra Jarrell Ash Co. (pris US \$ 28.500, -), et meget følsomt og fleksibelt instrument som gir alle nødvendige data for det emitterte lys. (En parallell oppstilling bestående av samme type katoderør med et enklere instrument for lysmåling blir brukt for testing av lampefosforer).

Foruten testingen av TV-fosforer for farge og effektivitet utføres forskjellige andre målinger, som f.eks. decay time, magnetisk suscpetibilitet, emisjons- og eksitasjonsspektra, elektronspinnresonans, etc. dessuten måles pulverkarakteristika som partikkelstørrelsesfordeling og BET-overflate.

Et laboratorium for mer fundamentale undersøkelser av luminiscensfenomenet var meget godt utstyrt med avanserte instrumenter. Et Hitachi MPF-2A Fluorescens Spectrophotometer ble fremhevet som spesielt følsomt.

Utvalget av analyseinstrumenter var også meget godt. Det fantes to vanlige emisjonsspektrografer og en "Direct Reader" fra Jarrell Ash Co., denne ble hovedsakelig brukt for legeringsanalyser. Dessuten to-tre røntgendiffraktrometre, hvorav ett for høytemperaturmålinger, ett instrument for "X-ray optical fluorescence" (XOF), tre eller fire instrumenter for atomabsorpsjon/flammefotometri (Jarrell Ash, Perkin-Elmer). En interessant variant av sistnevnte analysemetodikk var direkte fordamping av faste prøver, som ble bragt inn i flammen i små nikkeldigler. Prepareringen av prøver for XOF-metoden omfattet

oppløsning i salpetersyre, inndamping og kalsinering til oksyd, og gløding av dette ved  $1100^{\circ}\text{C}$  for å gi en finkrystallinsk prøve. Denne ble så presset i en metallramme (uten tilsats av bindemiddel) og analysert. Vanligvis ble Eu tilsatt som intern standard. Forøvrig ble det det dessverre ikke tid til å gå i detaljer angående analysemetodene.

Av utstyr forøvrig kan nevnes elektronmikroskop (Nordel), flere instrumenter for bestemmelse av gasser i metaller (Leco), IR-spektrografer, Auto-Analyzer, m.m. Dessuten rikelig utstyr for metallografi og andre fysikalsk-metallurgiske undersøkelser. Vi ble vist forsøk med sone-smelting hvor raffineringsgraden ble forsterket ved å sende likestrøm gjennom prøven. Vi så også fremstilling av store germanium enkrystaller.

I et laboratorium for væske-væske-ekstraksjon var Dr. Kim (som tidligere har samarbeidet med Tor Stensland) i gang med utvikling av en ekstraksjonsprosess for rhenium. Han brukte små mixer-settlere i glass, levert av Denver Equipment, av samme type som er bruk ved Hazen Research og Colorado School of Mines. Det var 5 - 6 ekstraksjonstrinn, et par scrub- og strip-trinn. Ekstraksjonsmidlet var Adogen 464. Prosessen var grei, ifølge Dr. Kim, som tidligere har utviklet væske-væske-ekstraksjonsprosesser for raffinering av W og Mo. Disse er nå i drift i fabrikk, men det ble dessverre ikke anledning til å se den delen av anleggene.

I våre diskusjoner om testing av fosforer og råmaterialer for fosforer ble det understreket fra Sylvania's side at det ikke kan gis entydige kriterier for et tilfredsstillende "phosphor grade" oksyd. Sylvania må gjennomføre sin test-prosedyre, inklusive "production test" for å avgjøre om et produkt er tilfredsstillende eller ikke. Renheten er viktig, men åpenbart ikke den eneste avgjørende faktor. Det ble nevnt at et 99,9%  $\text{Y}_2\text{O}_3$  kan være et tilfredsstillende råstoff, mens et såkalt 99,99% oksyd kan være for dårlig. (Sylvania la øyensynlig ikke så stor vekt på det oppgitte antall niere).

Vi fikk inntrykk av at våre ressurser og kompetanse på analyseområdet kan anses som tilstrekkelige, og at spesielt vår massespektrometriske metode synes velegnet for analyse av "superrene" produkter. Vi ble

imidlertid frarådet å legge for mye arbeid i fremstilling og testing av fosforer. Den eventuelle kjøper (f. eks. Sylvania) vil i alle fall måtte gjennomføre sin test-rutine, og våre egne resultater vil lett kunne føre oss på villspor og lede til uoverensstemmelser. Sylvania har tidligere hatt dårlige erfaringer med oksydleverandører som selv har testet sine produkter. En viss grad av kvalitetskontroll i form av enklere fluorescensmålinger ville de imidlertid ikke fraråde. For mer kvalitative bedømmelser brukte de selv også UV-lamper ("Mineralights" fra Fischer Scientific), og de viste oss en enkel innretning for gnist-eksitasjon som de mente vi kunne ha nytte av. Prøver blir her plassert i et glassrør, og etter evakuering blir den eksitert ved hjelp av en gnist under røret. På denne måten oppnås en emisjon som ligger forholdsvis nær opp til den man får i et katoderør.

### 1.3. Omvisning i fabrikk

3. november ble vi vist rundt i en del av produksjonsanleggene av Mr. Richard Doepker, production plant manager. Vi så først anlegget for fremstilling av TV-fosforer -etter sigende verdens største i sitt slag. Råstoffene for alle fosforene er oksyder (av zink, cadmium, yttrium osv.). De blå og grønne fosforer består av henholdsvis zink-sulfid "dopet" med sølv og zink-cadmiumsulfid (ca. 10% Cd) "dopet" med kopper. Etter oppløsning av oksydene i store glassbelagte tanker fjernes forurensningene ved utfelling, deretter felles sulfidene ut med  $H_2S$ . Etter filtrering og tørking kalsineres sulfidene i spesielle "fluxer" og under spesielle atmosfærer -dette er det mest kritiske prosessstrinn.

Det røde fosforet består av Eu-dopet yttriumoksyd. Sylvania har tidligere laget andre typer, som f. eks. vanadat, og oksyd med B-tilsetning, men lager nå bare den rene oksydyten. Det ble påstått at dette er vanskeligere å lage enn f. eks. vanadat, men gir bedre resultater. Ifølge Mr. Doepker lager ingen av fosforprodusentene lenger rødt fosfor basert på yttriumvanadat, muligens med unntagelse av Derby Luminescent. RCA, den nest største produsenten i USA, lager Eu-dopet Y-oksidsulfid, det samme gjelder Philips. General Electric, USA, lager forholdsvis små mengder rødt fosfor på  $Gd_2O_3$ -basis.

Erstatter Gd Eu eller Y ?

Også ved fremstillingen av det røde fosfor er første prosesstrinn oppløsning av oksydene, her i tanker av syrefast stål. I dette tilfelle trenges ingen raffinering <sup>x)</sup>, yttrium og europium kopresipiteres som oksalat og kalsineres til oksyd. Deretter følger gløding ved høy temperatur (2200 °F) i en spesiell flux. Dette er igjen det mest kritiske prosesstrinn (glødetid, temperatur, fluxens sammensetning). Glødingen foretas i digler av "high density alundum". Det glødete produkt finmales (- 400 mesh) og slemmes opp i vann for å fjerne overskudd av flux. I enkelte tilfelle tilsettes også en "coating". Etter filtrering og tørking er så fosforet ferdig.

Vi fikk også se produksjonen av hullmasker (aperture masks) for TV-apparater. Maskene lages av rustfritt stål, som mates kontinuerlig inn i produksjonslinjen i båndform. Etter vasking og etsing får stål-båndet et belegg av fiskelim (muligens av norsk opprinnelse?) tilsatt kaliumkromat. Deretter går båndet til eksponering, som resulterer i at belegget fikseres der hvor det belyses, dvs. overalt bortsett fra der hullene skal være. Belegget over hullene løses bort, deretter etses hullene med en jernklorid-løsning. Antall hull pr. maske er 440 000. Hver enkelt maske kontrolleres grundig. Det er to produksjonslinjer, den mest automatiserte kan alene produsere ca. 10 000 masker pr. dag.

Sylvania produserer ikke TV-rør i Towanda. Mr. Doepker fortalte om denne produksjonen at skjermene for farge-TV i tur og orden belegges helt med de respektive fosforer (tilsatt polyvinylacetat og kaliumkromat), prikkene fikseres ved eksponering gjennom hullmasken, og resten av belegget løses opp. Det foretas nå alltid gjenvinning av det ubrukte fosfor. F. eks. vil det gå med 12 - 15 g rødt fosfor for å dekke en 25" skjerm, men bare 2 - 3 g blir sittende igjen i form av "røde prikker". Resten blir gjenvunnet.

---

x)

Imidlertid hender det at det på forhånd foretas "upgrading" av  $Y_2O_3$  som ikke er tilstrekkelig rent, f. eks. ved fjerning av Ce.

Sylvania har også sitt eget anlegg for fremstilling av  $Y_2O_3$ . (Prof. Gumps prosess), men finner det for tiden ikke regningssvarende å drive dette.

2. NOTATER FRA MØTE I NEW YORK 30. OKTOBER 1970  
ANGÅENDE PATENTSPØRSMÅL

Møtet fant sted på advokat Lucas' kontor. Foruten W.D. Lucas deltok advokat D. L. Just samt O. Braaten og B. Gaudernack. Hensikten var å diskutere en eventuell patentsøknad i USA for den ekstraksjonsprosess for yttrium, basert på kvaternære ammoniumforbindelser som ekstraksjonsmiddel, som er utviklet ved IFA. Advokat Lucas hadde på forhånd fått tilsendt en engelsk oversettelse av den norske patentsøknaden.

Gaudernack ble orientert om den siste utvikling i saken, bl. a. om at granskingen i Norge hadde bragt frem US patent 3. 294. 494 som er nyhetsskadende for hovedpåstanden i vår patentsøknad. Diskusjonen dreide seg vesentlig om hvorvidt vår søknad kunne reformuleres slik at det likevel kan være håp om å få den gjennom. Mulighetene for å gå klar av "prior art"-patentene ved å spesifisere andre syrestyrker, saltkonsentrasjoner etc., synes små. Man var inne på at muligheten for å fjerne mesteparten av erbium i første prosesstrinn (nitrat-ekstraksjonen) kanskje kunne utnyttes. Det ble også antydnet at kombinasjonen av de to prosesstrinn i en bestemt rekkefølge (nitrat-tiocyanat) kunne være patenterbar.

Lucas' konklusjon og anbefaling var imidlertid at vi bør spille på at vår prosess gir yttrium av meget høy renhetsgrad, mens de tidligere patenter bare antyder forholdsvis grove separasjoner. Vi bør med andre ord formulere en patentsøknad som gjelder en kombinasjon av de to ekstraksjonsprosessene, spesifisert helt entydig for fremstilling av superrent yttriumoksyd.

Vi ble også enige om at advokat Lucas skal få tilsendt en kopi av vårt foreslåtte innlegg ved "ISEC-71" angående de matematiske modeller av Aliquat/nitrat-prosessen. Han vil gi en kommentar til de patent-tekniske aspekter ved eventuell publisasjon av innlegget.

3. NOTAT FRA MØTE MED SAMINCORP INC., NEW YORK,  
30. OKTOBER 1970

I anledning den forespørsel Megon sendte Sudamin på 1 tonn xenotim telegraferte de undertegnede i London og ba om møte i New York, kfr. vedlagte kopi av telegrammer.

I møtet 30. oktober deltok:

fra Samincorp Inc., M.H. Herzfeld, vice-chairman

" " " herr Hirschfeld

fra Megon B. Gaudernack

" " O. Braaten

Samincorp er del av samme gruppe som Sudamin, kfr. trykksaker mottatt under møtet i Brussel for 3 år siden.

Samincorps tilbud lyder på \$ 5,30 pr. lb  $Y_2O_3$  cif Oslo m/min 25%  $Y_2O_3$ . Vi fortalte dem at vår selvkost er ca. \$ 3 pr. lb og at det følgelig var hva vi var interessert i å kjøpe det for (eller mindre).

Herr Herzfeld forklarte at de var svært lite interessert i leveranser på så lite som 1 tonn. De ville gjerne gjøre avtaler for 10 - 20 - 30 eller 50 tonn og da gjerne fordelt med volumet stykket opp i månedlige leveranser på tilsvarende 1 - 2 - 3 eller 4 tonn osv. I så fall ville prisen bli fullt konkurransedyktig med hva vi kunne produsere det for. (Lavere enn for \$ 3 pr. lb).

Deres betingelser var forskjellige fra Derby & Co.'s i to henseende:

1. Derby's pris er i henhold til analyse ved A. Knight's laboratorium. Sudamin's tar hensyn til sin egen og kjøperens og avtaler en oppmann i tvilstilfeller (når det er forskjell).
2. De krever 80% cash ved kjøp mens Derby krever 90%. I tilfelle avtale for større volum fordelt over et år som nevnt ovenfor, betaler vi pro rata, etter som det blir levert.

Vi drøftet kort muligheten for betaling med produsert  $Y_2O_3$  for xenotim. De var lite interessert og måtte i tilfelle ha full eksklusivitet for et område f. eks. USA. Av andre råmaterialer nevnte de 60% konsentrat fra Australia og fra Canada. Prisen på dette lå i området \$ 6 - 9 pr. lb  $Y_2O_3$ . De kunne også skaffe yttriumkarbonat av ennå høyere renhet, selvsagt til høyere pris. Råmaterialer for europiumoksyd ble også diskutert, og de nevnte at et konsentrat som inneholder 0,2 - 0,4% Eu (eller mer) kan anses som interessant. De forsikret oss at råmaterialer

for  $Y_2O_3$  produksjon ville aldri være et problem. Derimot var salg av  $Y_2O_3$  som produkt vanskelig. Prisen ligger på \$ 28 - 32 pr. lb avhengig av mengde og kvalitet. Det er bare tre-fire kunder i USA:

Sylvania

RCA

GE

Radium Corp. of USA (?)

Det er et visst marked for metallisk yttrium ingot, men det er lite.

Vi lovte å svare dem på deres forskjellige antydninger og forslag i henhold til dette møtet og telegrafisk tilbud, når vi har fått vurdert situasjonen på basis av denne rapport.

20.11.70

## COPY TO

Eg 31. Salalah  
9 miles  
Feb.

SAMPLE  $\frac{1}{2} O_3$

DATE REC'D 10/28/70

DATE COMPLETED 11/2/70

| LOT NO.   | PRICE |
|-----------|-------|
| EA/95/F-2 | 4     |

☐ PHOTO EMISSION  
☐ DIRECT READER  
☐ X-RAY FLUOR.  
☐ XOF  
☐ IR

- ☐ A.A.-FLAME EMISSION
- ☐ CHROMATOGRAPHIC
- ☐ COMBUSTION
- ☐ GRAVIMETRIC
- ☐ INERT FUSION

- ☐ POTENTIOMETRIC  
☒ SPECTROPHOTOMETRIC  
☐ TITRIMETRIC  
☐ VACUUM FUSION  
☐ OTHER

ANALYST

APPROVED BY:

J. M. L. L.

DATE REC'D 10/16/74

DATE COMPLETED 2/28/70

 $\gamma_2 O_3$ [illegible]

APPROVED BY

BY John H. Smith

J. Nielsen

☐ OTHER

XOF

[DATE REC'D]

/ /

DATE COMPLETED 10/28/70

## SAMPLE

$$Y_2O_3$$
$$(\mathbb{C}[x_1, \dots, x_n] / (N))^{(1)} \cong \mathbb{C}[x_1, \dots, x_n] / (N) \quad \text{if } (N) \text{ is a prime ideal,} \\ (\mathbb{C}[x_1, \dots, x_n] / (N))^{(1)} \cong \mathbb{C}[x_1, \dots, x_n] / (N) \oplus \mathbb{C}[x_1, \dots, x_n] / (N) \quad \text{if } (N) \text{ is not a prime ideal.}$$
REMARKS:

ANALYST

Chiswell

APPROVED BY

# SYLVANIA ELECTRIC PRODUCTS INC.

COPY TO:

CHEMICAL & METALLURGICAL DIVISION

TOWANDA, PENNSYLVANIA 16818

*J. Miller*

## SPECTROGRAPHIC QUALITATIVE ANALYSIS REPORT

| PLATE NO.      | DATE RECEIVED | DATE OF ANALYSIS | SAMPLE |
|----------------|---------------|------------------|--------|
| 5042<br>5741   | 10/16/70      | 10/23/70         | Y203   |
| Ag             | VF            |                  |        |
| Al             | VF            |                  |        |
| As             |               |                  |        |
| B              |               |                  |        |
| Ba             |               |                  |        |
| Be             |               |                  |        |
| Bi             |               |                  |        |
| Cd             | FT+           |                  |        |
| Ce             |               |                  |        |
| Cr             | VF+           |                  |        |
| Cu             | VF            |                  |        |
| Fe             | VF+           |                  |        |
| Ge             |               |                  |        |
| Mg             | FT            |                  |        |
| Mn             | VF            |                  |        |
| Mo             |               |                  |        |
| Nb             |               |                  |        |
| P              |               |                  |        |
| Pb             | VF            |                  |        |
| Sb             |               |                  |        |
| Si             | VF            |                  |        |
| Sn             |               |                  |        |
| Str            |               |                  |        |
| Ta             |               |                  |        |
| Th             |               |                  |        |
| W              |               |                  |        |
| Zn             |               |                  |        |
| V              |               |                  |        |
| V <sub>2</sub> | VF            |                  |        |
| V <sub>3</sub> | FT            |                  |        |
| V <sub>4</sub> |               |                  |        |

REMARKS

ANALYST

APPROVED

SYMBOL

PPM - RANGE

SYMBOL

% RANGE

BLANK SPACE -  
ELEMENT SOUGHT BUT  
NOT DETECTABLE

VF  
VF+  
VF  
FT  
FT

< 1  
0.5-5  
1-10  
10-100  
100-500

T  
T+  
ST  
ST  
ST  
ST  
ST

0.01-0.1  
0.05-0.5  
0.1-1.0  
0.5-5  
1-10  
10-100  
100-1000

## RAPPORT FRA STUDIEREISE I USA

Reisetid: 4. - 13. 11. 1970.

Deltagere: Overing. Orvar Braaten og berging. Odd Eidsmo. *Som har skrevet rapporten*

Formål: Kontakte personer og institusjoner som kunne tenkes å ha kompetanse til å utføre flotasjonsforsøk med malmprøver fra Fensfeltet med henblikk på oppkonsentrering av SJ-mineraler.

Dette er forøvrig foreslått av dosent M. Digre i hans "Notat for Forskningsgruppe for Sjeldne Jordarter. - Oppredningsundersøkelser vedr. Fensfeltet", datert 8. januar 1970.

I denne forbindelse nevner Digre følgende laboratorier i USA:

American Cyanamid, Stamford, Conn.  
Denver Equipment Co., Denver, Colo.  
Galigher Co., Salt Lake City, Utah.

Forberedelser: De tre ovennevnte institusjoner ble kontaktet pr. brev datert 2. 10. d.å. hvor det ble spurt om våre representanter kunne komme over for å diskutere forsøksprogram og økonomisk ramme for arbeidet. Og meddelte at i fall vi fikk lov å komme ville vi på forhånd flysende malmprøver til orientering og diskusjonsgrunnlag for vårt besøk.

Brevene ble vedlagt notat fra Digre, "Fen Carbonatite Ore - Mineral Dressing - Geology - Mineralogy", datert 18. september 1970.

I notatet er det kort summert hva som er utført av oppredningsforsøk opp til nå og konkluderer med at flotasjon ser ut til å bli mest aktuell som oppredningsmetode for denne malmtypen. Notatet vedlegges som bilag 1.

Samtlige svarte positivt på vår henvendelse.

Denver gjorde oppmerksom på at de ikke kunne utføre slike oppdrag selv, men ville sette oss i forbindelse med Hazen Research som de benytter i slike anledninger.

Reiserute med oppgitt tidsrom for vårt besøk ved de respektive institusjoner ble sendt over og fikk bekreftet at vi var velkomne og at det oppgitte tidsrom passet for dem.

Som oppgitt ble nå prøver sendt over og disse ble splittet ut fra cand. real. Sæbø's prøve fra Vegskjæringsmerket II B.

Til hver av de ovennevnte ble sendt en ubehandlet prøve på ca. 200 g knust til - 1" og en prøve av bordkonsentrat, som også var tatt ut fra II B og malt til - 0,5 mm før bordvaskingen.

Prøveprepareringen ble besørget av Krogh.

Videre tok vi med oss prøver av fire forskjellige SJ-førende mineraler som var fremstilt av Sæbø.

Disse prøvene samt en mineralogisk beskrivelse fra Sæbø ble overlevert samtlige vi besøkte. Denne beskrivelse vedlegges som bilag 2.

Jeg møtte Braaten i New York og den 6. 11 reiste vi ut til:

American Cyanamid Co.  
Mining Chemicals Department  
1937 West Main St.  
Stamford, Conn. 06904 - Telf. 203 - 7331.

Der møtte vi Mr. R. B. Booth, director of Research for Mining Chemicals Department, Mr. Arnold Day, Group Leader (oppredningsmann) og Mr. F. W. Farwall (mineralog).

Braaten redegjorde for hensikten med vårt besøk og ga en orientering om hva Megon stod for.

Mr. Farwall hadde foretatt en orienterende undersøkelse av vårt bordkonsentrat.

Etter separasjon av prøvene i tung væske med sp. v. 3,3 hadde han tatt synkefraksjonen og malt til 270 mesh (53 micron). Deretter fraksjonert prøven og studert de forskjellige fraksjoner i mikroskop.

Mr. Farwall's konklusjon for disse undersøkelsene var at SJ-mineralene var meget finfordelt først og fremst som inneslutninger i ankeritten.

Mr. Day bemerket at innholdet av SJ i prøven var meget lavt (oppgitt til 2 - 3%) og nevnte at rågodset i Mountain Pass holdt ca. 12%.

Etter denne innledningen ble vi vist rundt i laboratoriene og disse var bra utstyrt for kjøring av oppredningsforsøk i benkeskala. Analysearbeidet i forbindelse med oppredningsforsøk var de bra utstyrt for å utføre mineralogiske, våtkjemiske og røntgenanalyser.

På vårt primære spørsmål om de var villig til å påta seg oppdrag for oss gjorde de oppmerksom på at de først og fremst var innstilt på å gjøre forsøk for store flotasjonsverk som var i drift. Dette med henblikk på salg av reagenser.

Et anlegg med påsettning ca. 1000 tonn pr. dag, som antydnet for Fæn, fant de lite interessant. Men de lovte å overveie saken og komme tilbake pr. brev.

./.

Vi har mottatt brev fra de som er datert 16.11, se bilag 3, og på grunnlag av våre samtaler, er det overraskende at de tilbyr å kjøre et orienterende forsøk for oss, og de gjør oppmerksom på at de ikke beregner betaling for slike forsøk.

På spørsmål om de hadde spesielle reagenser for flotasjon av SJ-mineraler var svaret nei. De nevnte at deres 600-serie kunne være aktuell som trykker for karbonater i denne forbindelse.

Etter weekend reiste vi over til Denver og kom dit søndag 7.11, kl. 19. Mandag morgen oppsøkte vi:

Denver Equipment  
600 Broadway  
Denver, Colorado 80203  
Telf. (303) - 244 - 4466.

Vi ble her mottatt av Mr. R. E. Hancock, Field engineer.

Etter orientering og diskusjon om leveranse av tilleggsutstyr for flotasjonssellene på Megons anlegg på Glamsland ble det fastlagt program for vårt besøk. Mandag etter lunsj skulle vi besøke:

Hazen Research, Inc.  
4601 Indiana Street  
Golden, Colorado 80401  
Telf. (303) - 279 - 4501

og tirsdag skulle vi ut til

Colorado School of Mines Research Institute  
P. O. Box 112  
Golden, Colorado 80401  
Telf. (303) - 279 - 2581.

Hos Hazen ble vi møtt av Dr. Hazen, direktør, Mr. Pablo Hadzeriga, senior process engineer og Dr. Roland Schmidt, mineralogist.

Hazen Research ble startet i 1961 og er basert på å ta oppdrag for industrien og dekker følgende felt:

1. Mineral oppredning.
2. Hydrometallurgi.
3. Utvikling av flowsheet og Engineering.
4. Geologi og geokjemi.
5. Computer service.
6. Mineralogi.
7. Analytisk kjemi.
8. Kjemisk prosessforskning og utvikling.
9. Forberedende kapital og driftsomkostninger.
10. Forurensnings-kontroll.

Etter gjensidig orientering ble vi vist rundt i laboratoriene og disse var meget bra utstyrt, spesielt hadde de allsidig utstyr for kjøring av forsøk i pilotskala.

Det var montert flere driftsklare pilotanlegg for kjøring av forskjellige oppredningsprosesser og det var lagt stor vekt på hydrometallurgiske prosesser.

Utstyret for analysering virket stort sett nytt og moderne.

Prøvene fra oss hadde de ikke studert nærmere og diskusjonen om vårt oppredningsproblem ble først og fremst viet den mineralogiske side av saken.

De la stor vekt på dette og for at de kunne bli bedre kjent med mineralogien i Fæn foreslo Dr. Hazen at Dr. Schmidt kom over til Norge for å studere forholdene i marken og bli orientert om de undersøkelsene Sæbø har under arbeide.

I brev av 13. 11 bekrefter Dr. Schmidt at han kommer til Oslo 22. 11 d. å. og eventuelle forhandlinger om utførelse av forsøk hos Hazen Research vil bli avhengig av tilbud de kommer med etter at Schmidt har vært her.

./.

Dr. Schmidt's brev vedlegges som bilag 4. Dr. Schmidt var her i forrige uke og forstår at hans besøk blir rapportert av Sæbø.

Ved vårt besøk hos Colorado School of Mines Research møtte vi Dr. Herman Ponder, Director of Research Mining Division, Mr. A. P. Herring, Manager Chemical Division, og Mr. R. C. Merritt, Manager Metallurgical Division.

Dette instituttet eies av staten og ble startet i 1949 og drives som en selvstendig institusjon uavhengig av Colorado School of Mines.

Instituttet har stort sett opplegg og fagområde som Hazen Research og er basert på oppdrag fra industrien og staten.

Under omvisningen ble vi vist utstyr for kjøring av forsøk i benkeskala og det var i det hele montert fem pilotanlegg for kjøring av forskjellige prosesser.

Siden transport av mineralkonsentrater i rørledning stadig får større utbredelse nevnes at vi så deres forsøksanlegg for hydraulisk transport av mineraler.

CSOM Reserach Institute har avgjort den lengste erfaringen i oppredning av SJ av de vi kontaktet der borte.

Mr. Merritt som var vår omviser førte også de generelle diskusjoner med oss og han viste meget stor interesse for vårt problem. Dette fremgår forøvrig av Mr. Merritt's bekreftelse på vår diskusjon i brev datert 13. 11, se bilag 4.

I brevet redegjøres for hvordan han vil legge opp et preliminært forsøksprogram og anslår dette til ca. 1 måneds varighet og vil koste \$ 7000 - 8000.

Vi kom over en artikkel i CSOM Mineral Industries Bulletin for mars 1969 som vedlegges som bilag 5. Artikkelen heter "The Rare Earths Today", og den gir en interessant oversikt over SJ-mineraler, oppredning, videreforedling og anvendelse av disse.

Fra Denver reiste vi til Salt Lake City hvor vi besøkte

The Galigher Company  
545 - 585 West Eight SO. - P. O. Box 209  
Salt Lake City, Utah.  
Telf. (801) 359 - 8731, Telex 038 536.

Vi møtte her Mr. H. E. Wright, President, Mr. Helmer A. Johnson, Manager - Metallurgical Sales, Mr. H. A. Dawson, Metallurgist (laboratoriesjef) og Mr. Bryant J. Bullen, Metallurgical Engineer.

Galigher har ca. 250 ansatte og lager maskinutstyr først og fremst for oppredningsanlegg. Deres hovedprodukter er flotasjonsmaskiner og pumper og Galigher er mest kjent for sin Agitair flotasjonsmaskin som bygges med tankvolum opp til 300 cu. ft. Denne maskinen har bl. a. den fordel at den kan behandle forholdsvis grovt gods.

Både flotasjonsmaskiner og spesielt pumper har stort behov for reservedeler så en meget betydelig del av Galigher's produksjon kommer fra denne sektor.

Ved siden av at Galigher yter konsulenthjelp til sine kunder på det tekniske område bistår de også med "Research Services", bl. a. ved kjøring av flotasjonsforsøk i benkskala i sitt laboratorium i Salt Lake City.

Etter gjensidig orientering ble vi vist rundt i laboratoriet og verkstedene. Laboratoriet for oppredningsforsøk var meget enkelt både når det gjaldt utstyr og lokaler.

Ved nærmere diskusjon om vårt problem, hvor Mr. Johnson var den mest fremtredende, fikk vi inntrykk av at disse folkene var mere innstilt på å gå rett på sak for å undersøke muligheten for oppredning av en malm med enkle forsøk.

Det fremgår av Galighers bekreftelse på vårt besøk i brev datert 13.11, se bilag 6, at omkostningene ved forsøk hos de er såvidt billig som ca. \$ 1000 pr. mnd.

På grunnlag av de timesatser de beregner for sine ingeniører tilsvarende dette riktignok bare en manns innsats i 80 - 90 timer pr. mnd., men det må regnes for å være rimelig i allefall.

### Konklusjon

Som nevnt innledningsvis var hensikten med denne turen å få kontakt med et institutt eller firma som hadde kompetanse til å ta på seg oppredningsforsøk med Fæn-malmen.

Når det gjelder American Cyanamid må vi iallfall benytte oss av deres tilbud, men vi kan ikke regne med at de kan påta seg forsøk for oss utover det innledende forsøket som de utfører gratis.

Hazen Research og Colorado School of Mines Research Institute viste meget stor interesse for denne oppgaven og begge er meget interessert i oppdrag fra oss.

Jeg går ut ifra at det eventuelt ikke vil komme på tale å engasjere mere enn en av de, og hvem vi i tilfelle burde velge er ikke lett å avgjøre på grunnlag av inntrykk fra et såvidt kort besøk.

Hvis en først gir disse to institusjoner et oppdrag må en regne med å satse et beløp på minst n. kr. 50.000, men det er neppe riktig å ta standpunkt til dette før vi får resultatene fra Sæbø's mineralundersøkelser og analysene av borkjernene fra siste sommers borer i feltet.

Jeg ser ikke bort i fra at det kan være riktig å regne med at det på litt lengre sikt kan komme på tale å benytte seg av den erfaringen disse to forskningsanstaltene sitter inne med om SJ.

Med hensyn til Galigher stiller saken seg noe anderledes da de er innstilt på å kjøre et orientert forsøk som ikke koster mere enn ca. nr. kr. 7.000, -.

I første omgang vil det da bli tale om å sende prøver til American Cyanamid og Galigher Co., og så snart ovennevnte analyser foreligger bør vi ta standpunkt til dette.

Med hensyn til ovennevnte analyser som er under arbeide vil jeg presisere så sterkt jeg kan at det er resultatene fra disse undersøkelser som må danne grunnlaget for vurdering av videre oppredningsforsøk med Fen.

Gjennom borkjerneanalysene får en et representativt kjennskap til råmalmene i et bestemt område og Sæbø's undersøkelser av SJ-innholdet i mest mulig rene mineraler gir opplysninger om hvilke oppkonsentreringer en kan regne med ad mekanisk vei.

Uten kjennskap til disse faktorer vil man mere eller mindre arbeide i blinde.

Trondheim, 2. 12. 1970

Odd Eidsmo

OE/kk  
4. 12. 70

22. 09. 70

Marcus Digre

Associate Professor in Mineral Dressing

N.T.H., Trondheim, Norway

Sept. 18th, 1970.

Fæn Carbonatite Ore - Mineral Dressing.

Geology - Mineralogy.

The Fæn Carbonatite Complex is a very large pipe formation predominantly consisting of carbonatite rocks. The carbonatite is characterised by the occurrence of niobium (columbium) - and rare-earth - element - containing minerals. The northern part contains up to 0,4 %  $Nb_2O_5$  as pyrochlore, nom.  $NaCa Nb_2O_6F$ , and was mined for this mineral from 1950-1965. The southern part has less  $Nb_2O_5$ , usually about 0,1 %, but contains 2-3 % RE (rare earth element) - minerals which may be of economic interest.

The dominant minerals in the carbonatites are calcite and ankerite (ferruginous dolomite). It further contains 10-20 % silicates, (mica, chlorite, quartz etc,) and varying amounts of apatite, magnetite, hematite, pyrite and baryte. The RE-minerals comprises fluorocarbonates of the Bastnäsitt-Parisitt-Synchisitt group, monazite and orthite. The apatite also carries some RE, about 1 %. Nb is found as pyrochlore.

Most of the minerals have a grain size in the range from 0,5-0,02mm, but the hematite may occur as extremely fine grains scattered in the carbonates. The pyrochlore is reported as partly having a poikilitic structure.

4 samples of the ore that has been selected for the present investigations have been analysed at the Norwegian Geological Survey.

The composition was found to be inside following limits:

30-50 % Calcite, 30-50 % ankerite, 2-3 % RE-minerals, about 0,2 % pyrochlore and about 1 % each of pyrite, magnetite, hematite and apatite. The total RE content was in the range 1,3-1,6 % as element, with about 100 ppm Eu.

Mineral Dressing tests.

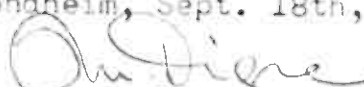
The Mineral Dressing Laboratory at NTH, Trondheim has done preliminary tests with gravimetric, electrostatic, h.i.-magnetic and

flotation methods, but so far with poor results. Gravimetric and magnetic methods will give a distinct RE-upgrading in the concentrates but recovery is at a low level, well below 50 %. The cause for this behaviour is probably the rather fine size of the RE minerals and the small differences in specific gravity and magnetic susceptibility compared to the rock minerals.

Flotation tests with various reagent combinations have so far not given any worthwhile separation between the RE-minerals and the calcite - ankerite which constitutes the main part of the ore. It is deemed essential as a first step to remove the bulk of these carbonates and produce a crude RE-concentrate, which can be further processed by mineral dressing, chemical or metallurgical methods. Flotation is still considered to be the most promising method to obtain such a crude concentrate, the negative results up to now notwithstanding. The small grain size and the brittleness of the RE-minerals works against the other mineral dressing methods, but should not have any important bearing on the flotation possibilities. The right type of attack on the problems would be to have a couple of laboratories with extensive flotation experience as a first step do an exploring investigation to try a wide range of flotation reagent combinations. If and when a promising approach is found, a second step should be a detailed study to find the optimal conditions and the limitations for the process. As a third step the method should be tried on different ore types.

The object of the investigations should be directed towards recovering the elements of economic interest, i.e. RE-elements (primarily Eu), Nb, Th and U. The RE-assays indicate a preponderance of light and intermediate RE-elements with smaller amounts of heavy RE-elements and Y.

Trondheim, Sept. 18th, 1970

  
M. Digre

associate professor

*Letter from J.A.W. Brögger*

On the mineralogy of the ankerite - carbonatites of the Fen Area.

The petrography and mineralogy of these carbonatites have been treated by J.A. Brögger (1921) and L. Sæther (1957). Since that time some new informations have been obtained, but the general picture of the petrography has not been changed very much.

Several other minerals have been identified and more complete ideas concerning the mineralogy, geochemistry and genetical relationships have been developed.

The carbonatites contain about 1.3 - 1.6 RE elements and it is of important economic significance to examine and understand the distribution of the various RE elements between all important mineral phases within the carbonatites.

Further, in order to attack all problems concerning the mineral dressing it is necessary to produce sufficient quantities of more or less pure concentrates of all important minerals for experimental works and chemical determinations. This work is in progress and we are able to present a small amount of more or less pure fractions of some minerals.

- No 1. The bastnäsite-group of minerals
- No 2. Orthite = (Allanite)
- No 3. Barite
- No 4. Celsian feldspar

The various concentrates are somewhat impure but the actual minerals are easily recognized in each sample.

Recent investigations in the Fen Area show that the field has been reheated and probably also recrystallized to some extent during the intense igneous activity in the Oslo Region in Permian time.

It is quite clear that a system of flat-lying joints combined with two set of vertical joints developed. These joints were healed by coarse grained calcite, barite, ironoxides and sulfides, crystals of the bastnäsite group of minerals, orthite, chlorite and montmorillonite. The influx of large amounts of silica, water and some heavy metal-fluorides caused the formation of large amounts of celsian feldspar, quartz, muscovite, orthite and some sulfides in the joints and in the massive carbonate rocks. These processes led to a redistribution of the thorium and rare earth content of the rocks.

At present we do not know exactly the technical and economic consequences of the Permian activity concerning the content of the thorium and rare earth minerals in the ankerite carbonatites of the Ben Area.

Blindern, 23. oktober 1970

  
Per Chr. Sæbe

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## THE RARE EARTHS TODAY

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### INTRODUCTION

An early Mineral Industries Bulletin (Williamson and Burgin, 1959) described the rare earths (lanthanons), covering the sources, occurrences, metallurgy, and uses of this interesting group of metals. Recent years have seen extensive changes in the rare earth industry, particularly in the large scale use of ion exchange and solvent extraction (liquid ion exchange) methods for separation and purification, and in the development of new and improved metal reduction techniques, so that large quantities of the pure rare earth metals and compounds have become available.

The more ready accessibility of these materials has been an expected catalyst in the development of many new applications, some of which already have become of industrial importance. The extent of the recent change in the rare earth industry is convincingly shown by the fact that consumption in the United States has grown from about 2,000 tons per year of rare earth oxides before 1965 to about 7,000 tons currently. These facts, together with the recent completion of a large rare earths processing plant in Colorado, made a new review of the subject seem appropriate at this time. This report accordingly will emphasize the newer processing techniques, and in particular will discuss some of the new and exciting applications of the rare earths.

As part of the tremendous growth in the industry, there has been a vast proliferation of the literature dealing with the rare earths and rare earth compounds and with new applications of these materials. It is not possible in a review of this type to examine all of the thousands of references; thus it is inevitable that some of the topics selected for discussion will not have been covered with the proper degree of thoroughness. It is hoped, however, that the areas which have been touched upon will prove to be interesting and

enlightening, and that the information presented will stimulate further consideration and discussion of this ever-changing and rapidly growing segment of the mineral industries.

The term "rare earths" is perhaps an unfortunate one, being both inaccurate and misleading. Actually the so-called rare earths are metals and not earths, and most of them are not rare. The name originated in the early days when some of the first materials separated were designated "rare earths" to distinguish them from the well-known and plentiful lime, magnesia, and alumina "earths." However, in spite of alternative names which have been suggested—lanthanons, lanthanide elements, and f transition elements—the old term "rare earths" still persists, and the Commission on Nomenclature of the International Union of Pure and Applied Chemistry has recommended that the term "rare earth metals" may be used for scandium, yttrium, and elements 57 through 71 (Chem. Eng. News, May 10, 1965). In this report the terms "rare earths" and "rare earth metals" will be used interchangeably to designate the metallic elements having atomic numbers from 57 to 71 inclusive, and including yttrium, but excluding scandium. Yttrium is in the same group (IIIB) of the periodic table as the rare earths, it occurs naturally with the rare earths and is prepared with them, and its chemistry is similar to that of the higher (atomic weight) rare earths. The symbols RE will be used for rare earth(s), and REO for rare earth oxide(s).

Table 1 following lists the rare earths, and table 2 shows their abundance in the earth's crust compared with a number of other metallic elements. It will be noted that cerium, the most abundant rare earth, occurs more widely than tin, cobalt, or molybdenum, and that thulium, the rarest of the rare earths, is more plentiful than cadmium, silver, gold or platinum.

TABLE 1.—*The rare earths*

| Name         | Symbol | Atomic number | Atomic weight    | Number of 4f electrons <sup>1</sup> |               |             |
|--------------|--------|---------------|------------------|-------------------------------------|---------------|-------------|
| Lanthanum    | La     | 57            | 138.91           | 0                                   | Cerium Group  | Light Group |
| Cerium       | Ce     | 58            | 140.12           | 1                                   |               |             |
| Praseodymium | Pr     | 59            | 140.91           | 2                                   |               |             |
| Neodymium    | Nd     | 60            | 144.24           | 3                                   |               |             |
| Promethium   | Pm     | 61            | 145 <sup>2</sup> | 4                                   |               |             |
| Samarium     | Sm     | 62            | 150.35           | 5                                   | Terbium Group | Heavy Group |
| Europium     | Eu     | 63            | 151.96           | 6                                   |               |             |
| Gadolinium   | Gd     | 64            | 157.25           | 7                                   |               |             |
| Terbium      | Tb     | 65            | 158.92           | 8                                   |               |             |
| Dysprosium   | Dy     | 66            | 162.50           | 9                                   |               |             |
| Holmium      | Ho     | 67            | 164.93           | 10                                  | Yttrium Group |             |
| Erbium       | Er     | 68            | 167.26           | 11                                  |               |             |
| Thulium      | Tm     | 69            | 168.93           | 12                                  |               |             |
| Ytterbium    | Yb     | 70            | 173.04           | 13                                  |               |             |
| Lutetium     | Lu     | 71            | 174.97           | 14                                  |               |             |
| Scandium     | Y      | 39            | 88.91            | 0                                   |               |             |

<sup>1</sup>Trivalent ion.<sup>2</sup>Isotope with half-life of 13 years.

### HISTORICAL BACKGROUND

The true beginning of rare earth history was in 1794 when Johann Gadolin, a Finnish chemist, found a new earth in a mineral which Arrhenius had discovered at Ytterby, Sweden, 6 years before. The discovery was confirmed in 1797 by Ekeberg, who suggested the names yttria for the oxide and gadolinite for the mineral. Both Gadolin and Ekeberg considered that the new oxide contained a single metal, although it was later learned that the original yttria was a mixture of oxides of at least 15 or 16 different metals. The chronology of discoveries of the individual rare earths is shown in table 3.

The rare earth industry is essentially a 20th century development, having had its origin in the late 1890's when the first rare earth products were obtained during the manufacture of thorium nitrate for the incandescent gas mantle industry. Carl Auer von Welsbach, an Austrian chemist, had found that the best mantle was composed of thorium oxide containing 1 percent of cerium oxide, which composition, incidentally, apparently is still in use. Monazite was the only common mineral with a reasonable thorium content, so it was selected as a raw material and a process was developed for extracting the thorium and making high purity thorium nitrate.

Monazite is actually a rare earth phosphate containing about 60 percent of rare earth oxides compared with only about 10 percent of thorium oxide. Recovery of the thorium therefore led to a large amount of by-product rare earths, about 10 pounds of rare earth oxides being formed for each pound of thorium produced. No uses were known for these

rare earths, other than the small amount of cerium nitrate used with the thorium in mantles. The rare earth industry thus began as a stepchild or by-product of the thorium industry, and this situation obtained for many years, leading to the accumulation of large stockpiles of rare earth concentrates. It is said that at the Camden, New Jersey, plant of the Welsbach Company, the rare earths actually created a disposal problem and were dumped into the river.

Monazite contains a mixture of the rare earth elements, in which lanthanum, cerium, praseodymium, and neodymium predominate, as shown in the representative composition:

|                  |     |
|------------------|-----|
| Lanthanum        | 22% |
| Cerium           | 46% |
| Praseodymium     | 5%  |
| Neodymium        | 18% |
| Samarium         | 2%  |
| Gadolinium       | 1%  |
| Yttrium          | 3%  |
| Other lanthanons | 3%  |

This mixture can be thought of as a single element of atomic weight about 110, since it undergoes normal chemical reactions with little change in composition and can be purified from non-lanthanoid impurities by standard chemical processes. It is thus understandable that the first uses were developed for this "mixed element". It should be mentioned that the difficulties in separation of the individual elements of this mixture were typical of the problems faced in the early days of rare earth chemistry.

TABLE 2.—*Abundance of rare earths and other metals*

| Name         | Symbol | Abundance<br>on earth<br>ppm* |
|--------------|--------|-------------------------------|
| Rare earths  |        |                               |
| Cerium       | Ce     | 46                            |
| Yttrium      | Y      | 28                            |
| Neodymium    | Nd     | 24                            |
| Lanthanum    | La     | 18                            |
| Samarium     | Sm     | 6.5 ✓                         |
| Gadolinium   | Gd     | 6.4                           |
| Praseodymium | Pr     | 5.5                           |
| Dysprosium   | Dy     | 4.8                           |
| Ytterbium    | Yb     | 2.7 ✓                         |
| Erbium       | Er     | 2.5                           |
| Holmium      | Ho     | 1.2                           |
| Europium     | Eu     | 1.1                           |
| Terbium      | Tb     | 0.9 ✓                         |
| Lutetium     | Lu     | 0.8                           |
| Thulium      | Tm     | 0.3 ✓                         |
| Other metals |        |                               |
| Nickel       | Ni     | 80                            |
| Copper       | Cu     | 70                            |
| Tungsten     | W      | 69                            |
| Tin          | Su     | 40                            |
| Niobium      | Nb     | 24                            |
| Cobalt       | Co     | 23                            |
| Lead         | Pb     | 16                            |
| Molybdenum   | Mo     | 15                            |
| Uranium      | U      | 4                             |
| Tantalum     | Ta     | 2                             |
| Mercury      | Hg     | 0.8                           |
| Bismuth      | Bi     | 0.2                           |
| Cadmium      | Cd     | 0.15                          |
| Silver       | Ag     | 0.10                          |
| Gold         | Au     | 0.005                         |
| Platinum     | Pt     | 0.005                         |

\* In igneous rock; averages of values given in several references.

The second stage in the growth of the rare earth industry saw a gradual spread of applications for the rare earth mixtures, together with a decline in thorium production as electrification developed. It was found in 1903 that the chloride of the mixture of rare earths could be electrolyzed to give the metal which was called mischmetal, that is "mixed metal." This material was pyrophoric, and when alloyed with iron found considerable use in lighter flints. This

usage still represents one of the larger tonnage applications of the mixed rare earths, the material being generally termed mischmetal today. The fluoride of the above mixed element was found in 1909 to have value in carbon arc lights, improving the brightness and color balance of the light, a use which has also persisted until the present.

Methods were developed for separation of cerium and lanthanum from the monazite residue, and the remaining material, enriched in praseodymium and neodymium, was called "didymium," since it was originally thought to be a single element. The term "didymium" is still used to some extent, primarily for the mixture of rare earths left after cerium is removed from the light (cerium group) rare earths, but also to identify the rare earth mixture left after both cerium and lanthanum are removed. Specially prepared oxides, particularly those high in cerium, found use as polishing materials, for example, for glass, and there was a small outlet for cerium and didymium in the manufacture of glass.

The rare earth industry thus originated and developed as an economically interdependent part of the thorium industry, involving the treatment of monazite to give thorium nitrate, mischmetal chlorides and fluorides, and very limited quantities of cerium, lanthanum, and didymium. This pattern continued essentially until the 1940's.

The third phase, from about the mid-1940's until about the mid-1960's, was marked by several significant developments. The first of these was the use of ion exchange separation techniques on a commercial scale, first reported from Iowa State College in 1947. This development made possible the production of pure RE materials on a large scale, and was a vast improvement over the tedious, time-consuming, and expensive chemical separations of the past.

A second development was the large Atomic Energy Commission (AEC) requirements for thorium as a fissionable source material during the late 1940's and early 1950's. Production of thorium from monazite for use in the AEC programs increased greatly, leading to enlargement of ore processing facilities, a search for new sources of the RE's, and intensified application research for the RE by-products which were being stockpiled. The suggestion from this research that there might be a large tonnage outlet for the RE materials in ferrous metallurgy was of major significance in leading to the commercial exploitation of the vast bastnaesite deposits in California, estimated to contain over 3 million tons of rare earth elements (on an oxide basis).

A third factor of significance in development of the RE industry was the aircraft nuclear propulsion project in about the mid-1950's. Large amounts of high purity yttrium were required in this program, leading to large-scale separations of the RE's.

By 1959-1960 it became apparent that there would be no immediate utilization of thorium as an atomic fuel element, and production was sharply curtailed. Also at about this time the production of thorium from Canadian uranium wastes was started, which ended the dependence of the thorium industry on monazite as a raw material. The Canadian Blind River-Elliott Lake conglomerate deposits contain an average of 2.5 pounds of  $U_3O_8$ , 1 pound of thorium, and 0.5 pound of RE's per ton of ore, all of which are now being recovered.

The present phase of the RE industry, starting in about the mid-1960's, has seen the production of large volumes

TABLE 3.—*Chronology of rare earth discoveries*  
(From Gschneider, 1964)

| Element      | Date of discovery | Discovered by                                                                       | Derivation of name                                                          |
|--------------|-------------------|-------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| Cerium       | 1803              | M. H. Klaproth, and by J. J. Berzelius and Wilhelm Hisinger, independently          | From asteroid Ceres                                                         |
| Lanthanum    | 1839              | C. G. Mosander                                                                      | From Greek word <i>lanthanein</i> , which means to be hidden or concealed   |
| Terbium      | 1843              | C. G. Mosander                                                                      | From the town of Ytterby, Sweden                                            |
| Erbium       | 1843              | C. G. Mosander                                                                      | From the town of Ytterby, Sweden                                            |
| Yttrium      | 1843              | C. G. Mosander                                                                      | From the town of Ytterby, Sweden                                            |
| Ytterbium    | 1878              | J. C. G. Marignac                                                                   | From the town of Ytterby, Sweden                                            |
| Samarium     | 1879              | Lecoq de Boisbaudran                                                                | From the Russian mine official, Colonel M. Samarski                         |
| Holmium      | 1879              | P. T. Cleve and independently by J. L. Soret                                        | From the Latinized word for the city of Stockholm, Holmia                   |
| Thulium      | 1879              | P. T. Cleve                                                                         | From the ancient name of Scandinavia, Thule                                 |
| Gadolinium   | 1880              | J. C. G. Marignac                                                                   | From the Finnish chemist, Johann Gadolin                                    |
| Praseodymium | 1885              | C. A. von Welsbach                                                                  | From the Greek words <i>prasios</i> and <i>didymos</i> , meaning green twin |
| Neodymium    | 1885              | C. A. von Welsbach                                                                  | From the Greek words <i>neos</i> and <i>didymos</i> , meaning new twin      |
| Dysprosium   | 1886              | Lecoq de Boisbaudran                                                                | From the Greek word <i>dysprositos</i> , meaning hard to get at             |
| Europlum     | 1889              | Sir William Crookes                                                                 | From the continent Europe                                                   |
| Lutetium     | 1907              | G. Urban (and independently by C. A. von Welsbach in 1908)                          | From the ancient name of Paris, Lutetia                                     |
| Promethium   | 1947              | J. A. Marinsky, L. E. Glendenin, and C. D. Coryell (in fission products of uranium) | From Greek mythology. Prometheus stole fire from heaven and gave it to man  |

of high purity RE's by means of ion exchange and solvent extraction (liquid ion exchange) processes, the development of important new applications, and the emergence of bastnaesite as the dominant raw material. In particular the development of the RE phosphors, starting in about 1963, which required very pure europium and yttrium oxides in unprecedented quantities, and concurrently the industrial use of liquid ion exchange to obtain pure separated RE's from bastnaesite, marked a profound change in the character of the industry.

Thus the rare earth industry, from its humble beginning as an unwanted stepchild of the thorium industry, has now become independent of thorium, which in turn has become a by-product of the rare earths. Any sizable demand for thorium for use in nuclear reactors appears to be still a decade or more in the future, and thorium requirements for

nuclear purposes are not expected to total more than a few hundred tons over the next 15 years. In fact, by-product thorium from the processing of monazite for RE's is now being accumulated, as the demand for the RE's exceeds that of the concomitant thorium. The rare earth ugly duckling has become a swan.

#### SOURCES OF THE RARE EARTHS

World and domestic sources and occurrences of the rare earths were covered thoroughly in the previous Mineral Industries Bulletin on this subject (Williamson and Burgin, 1959), and only a brief recapitulation will be given here.

The rare earths are widely distributed in nature, being found in over 160 minerals (Brit, 1964), but large commercially important deposits are comparatively few. The principal minerals are shown in the following tabulation.

| Mineral                                  | Type of ore     | Locations                                                                                       |
|------------------------------------------|-----------------|-------------------------------------------------------------------------------------------------|
| <b>Cerium group (Light rare earths)</b>  |                 |                                                                                                 |
| Monazite                                 | Phosphate       | India, Brazil, South Africa, United States, Australia, Malaya, Canada, Korea, Ceylon, Indonesia |
| Bastnasite                               | Fluorocarbonate | United States (California)                                                                      |
| <b>Yttrium group (Heavy rare earths)</b> |                 |                                                                                                 |
| Gadolinite                               | Silicate        | United States, Scandinavia, Germany, Ireland, Austria, Italy, Ceylon, Greenland                 |
| Xenotime                                 | Phosphate       | Scandinavia, Switzerland, Brazil, United States, Nigeria, Malaya                                |
| Euxenite                                 | Columbate       | Scandinavia, Madagascar, Brazil, Greenland, United States, Canada, Australia                    |
| Samarskite                               | Tantalate       | United States, Russia, Canada, Madagascar, West Africa                                          |

An interesting paper by Altschuler and others (1967) points out the possibility of doubling the domestic production of rare earths by recovery of these materials from apatite, as a by-product of phosphoric acid manufacture. Phosphate rock (containing apatite as the principal mineral) is mined extensively in Florida, Idaho, Montana, and North Carolina. The rare earths generally make up only from 0.01 to 0.1 percent by weight of marine apatite. However, the vast tonnages of apatite processed for the production of phosphoric acid make this source a substantial one for the rare earths if economical means of recovery can be found. In 1964 about 6 million tons of apatite was processed, containing nearly 3,500 tons of elemental rare earths. During the same year U.S. production of rare earth oxides was 2,300 tons. Altschuler and others suggest that present rare earth recovery techniques, such as ion exchange and solvent extraction, can be adapted to recover these materials from phosphoric acid processing.

Rare earths reportedly have been recovered on a small scale from apatite-rich rock in Finland (Chem. Eng., Jan. 2, 1967), and commercially in Russia and Poland (Brit., 1964). The apatite deposit on the peninsula of Kola (Russia) contains 0.5-5 percent of REO, and has been estimated to contain a potential reserve of 160 million tons of REO.

Analyses of the marine apatites were unusual (when compared with monazite and bastnasite) in showing cerium markedly depleted, being less abundant than lanthanum, and commonly less abundant than neodymium. This distribution appears to parallel that in sea water on the basis of very limited data, but is in conflict with a large body of rare earth analyses on phosphorite. Compared to conventional rare earth sources, the marine phosphorites appear to be unusually enriched in yttrium and in the middle and higher atomic weight rare earths such as europium, gadolinium, thulium, and erbium.

The enrichment in heavier elements is shown by comparing the distributions of rare earths in marine phosphorite, monazite, and bastnasite ores. As given in table 4, the aggregate percentage of the total rare earths (rare earth less yttrium) contributed by the first four members (lanthanum through neodymium) is shown. The remaining rare earths (samarium through lutetium) thus typically aggregate 25 percent in phosphorites, 10 percent in monazites, and 5 percent in bastnasites. Based on 1964 production figures, approximately 21 tons of europium, 74 tons of gadolinium, and 11 tons of thulium were available for recovery from the apatite processed.

TABLE 4.—Distribution of rare earths in various sources

| Element | Weight percent in |          |             |
|---------|-------------------|----------|-------------|
|         | Phosphorites      | Monazite | Bastnasites |
| La      | 70-80             | 85-95    | 95+         |
| Ce      |                   |          |             |
| Pr      |                   |          |             |
| Nd      |                   |          |             |
| Eu      | 0.5-1.0+          | 0.0x-0.1 | 0.1±        |
| Gd      | 1-6               | 1.0-4    | 0.1-0.5     |
| Tm      | 0.3-0.6           | 0.1      | —           |

(From Altschuler and others, 1967)

## EXTRACTION AND SEPARATION OF THE RARE EARTHS

The similarity in chemical behavior of the rare earths has traditionally made their separation difficult and time-consuming. The first major advance over the old techniques of fractional crystallization and precipitation came with the advent of ion exchange, first reported in the late 1940's and used on a large scale from about the mid-1950's. The second, perhaps even more important development, was the commercial introduction of solvent extraction (liquid-liquid extraction, liquid ion exchange) in about the mid-1960's. All of the rare earth metals can now be obtained in high purity by using these new techniques alone or in combination.

The following methods are available for separation of the rare earths:

1. *Fractional crystallization.* This technique depends upon slight differences in solubilities of salts of the various rare earths. Crystallization from a solution of a mixture of these salts will give crystals composed largely of the least soluble salt; the mother liquor will be enriched in the most soluble. The degree of enrichment obtained in a single crystallization is very small, and thousands of crystallizations may be required to achieve desired separations.

2. *Fractional precipitation.* This method involves adding a precipitant to a mixture in an amount insufficient for complete precipitation. The first precipitate obtained will be richer in the element having the least soluble product; if this is removed and more precipitant added in steps, a series of precipitates can be obtained varying slightly in solubility. As with fractional crystallization, this method is tedious and the efficiency of separation is low.

3. *Methods based on valency differences.* Cerium (IV), samarium (II), europium (II), and ytterbium (II) usually can be separated from the trivalent rare earths by methods based on the differences in valence. Thus cerium is easily oxidized, and practically all methods for its separation are based on this fact, for example, by precipitation of the basic ceric hydroxide. Europium can be separated by reduction with zinc and precipitation as the insoluble europous sulfate. Electrolytic reduction through amalgam formation has been used for separations involving samarium, europium, and ytterbium.

4. *Ion exchange.* (See Callow, 1966; Klotz and Love, 1963; Lever and Payne, 1968; Powell, 1961, 1964; Winger and Lindstrom, 1968). The advent of ion exchange marked a giant step forward in separation of the individual rare earths. Basically ion exchange is a chromatographic technique for separating mixtures of ions by sorption of the ions from solution on a suitable ion exchange medium (for example, a column of ion exchange resin), followed by differential displacement of the individual adsorbed ions with an eluting solution. This is known as "displacement chromatography." Since all of the RE's are so similar chemically and are ordinarily of the same valence (plus three), it was not expected that ion exchange would be effective in achieving the desired separations.

The successful use of ion exchange for rare earth separations was made possible by the addition of a complexing agent to the solution. This agent forms stable compounds with the various rare earths, the important fact being that the stability of the RE complex depends largely on the size of the RE ion. Thus lanthanum, which is the largest ion, forms the least stable complex, and lutetium, the smallest RE ion, forms the most stable complex in solution. The ion exchange process as practiced with a complexing agent can be described most simply by referring to figure 1, taken from Gschneider (1964).

In the figure, (a) represents a column of ion exchange resin which has a readily replaceable (easily ionized) hydrogen atom, H. When a chloride solution containing a mixture of RE's is added to the top of the column, the RE ions, shown as A and B, are exchanged for the hydrogen ions on the resin. In the figure, (b) shows the RE ions replacing the hydrogen ions, and (c) shows the entire column loaded with the RE mixture of A and B ions. Because of their difference in size, these ions will have slightly different affinities for the resin.

When a solution containing a complexing agent is now added to the column, it will tend to displace first those ions which form the strongest complexes in solution, that is, the smaller ions, leaving on the resin the larger ions which form the weaker complexes in solution. During this exchange, ammonium ions from the complexing agent, shown in the figure as N, are adsorbed on the resin in place of B, the smaller RE ion. As shown in the figure, (d) represents the ion exchange column after some of the B ions have been complexed and removed in solution, leaving the A ions largely on the resin—a separation has thus been effected. After all the B (smaller) ions have been complexed, further treatment with the complexing solution will remove the A (larger) ions as shown in the figure (e), and the separated A ions can be collected as they leave the column. Finally, the resin containing only ammonium ions, shown in the figure as (f),

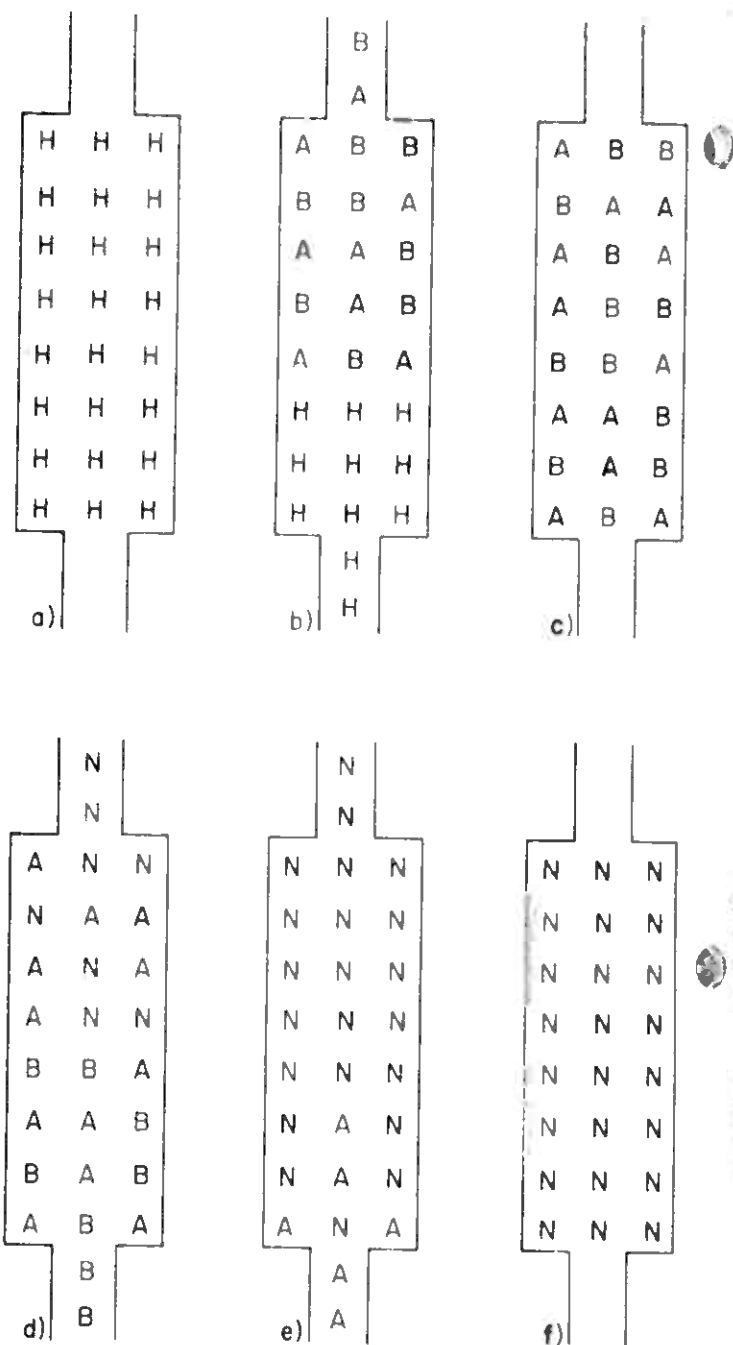


FIGURE 1—Schematic representation of rare earth ion exchange. (From "Rare Earths—The Fraternal Fifteen", Gschneider, 1964)

can be treated with acid to convert it to its original condition (a) and the sequence repeated.

It will be seen that in this process, those elements which formed the strongest complexes in solution gradually become concentrated at the leading edge of the RE band, and those which formed the weakest complexes at the trailing edge of the band, with all of the others between. The earths leave the bottom of the column in reverse order of their atomic numbers. The process is continued until the desired degree of separation is obtained, then the effluent solution collected in fractions containing the separated individual elements.

Ethylenediamine tetraacetic acid (EDTA) is a widely used complexing agent. The acid form of EDTA has a low solubility, so that if the resin is in the hydrogen form, the EDTA will tend to precipitate and block the bed. Accordingly, copper or iron, which forms a soluble complex with EDTA that is more stable than the rare earth complexes, is used as a "retaining ion" to load the column in front of the eluting solution. Lever and Payne point out that dysprosium-yttrium separation is very slow with EDTA because of the small difference in the stabilities of the two complexes. These two elements can be separated by elution with hydroxyethyl ethylenediamine triacetic acid (HEDTA) as there is a large difference in the stabilities of the HEDTA-Y and HEDTA-Dy complexes. HEDTA elution also works well for separating the light earths where EDTA is unsatisfactory because of precipitation in the column under the acid conditions necessary for good separation.

A recent Bureau of Mines publication (Winger and Lindstrom, 1968) reports on an investigation of amino acids as retaining agents, to replace hydrogen or copper, for rare earth separations with EDTA at 85-90° C. Hydroxyethyl ethylenediamine triacetic acid (HEDTA) and diethylenetriamine pentaacetic acid (DTPA) were the most effective of seven amino acids examined, allowing an increase of 75 percent in the EDTA eluant concentrations over that possible with hydrogen- or copper-retaining ions without precipitation taking place. Also, recovery of EDTA was easier than from the very stable copper chelate, an 85 percent recovery being effected before rare-earth break-through and during elution of lutetium, ytterbium, and thulium. Essentially complete recovery of the HEDTA or DTPA retaining agent was possible.

The principal advantage of ion exchange as practiced today is the ability to produce very high purity materials. Also, this technique is very versatile, so that changes from one product to another can easily be made. Disadvantages are said to be the discontinuous nature of the process, so that it is not well adapted to steady production on a large scale; limited capacity of the equipment (about five pounds of rare earth per cubic foot of resin); slow flow rates to permit satisfactory exchange of ions; the necessity of using very dilute solutions with currently available complexing agents; and a large necessary inventory of ion exchange resin. However, ion exchange production of rare earths is carried out on a large scale—Michigan Chemical Corporation is said to have 165 columns 2½ feet in diameter and 10 feet high where heavy RE's are separated by the ion. Smaller columns are used for separation of the less abundant earths.

5. *Solvent extraction.* (See Callow, 1966; Chem. Eng. News, Mar. 11, 1968; Lever and Payne, 1968; Peppard, 1961.) Solvent extraction (liquid ion exchange) as a possibility for separation of the RE's has been investigated since the 1930's, although it has only very recently been reported as being in commercial use.

In simplest terms solvent extraction involves the mixing of two immiscible liquids, an aqueous phase containing the chemical ions to be recovered, and an organic phase containing the extractant; that is, the ion exchanger in liquid form. During the extraction step, the desired ion migrates from the dilute aqueous phase (which may be impure) into the organic phase. This organic phase is then separated from the barren aqueous phase. In the stripping or removal step, the procedure is reversed and the desired ion passes from

the loaded organic into a new aqueous phase. Adequate mixing of the phases is important, as is ready separation into discrete layers after mixing. Mixing and settling tanks or countercurrent gravity-flow towers are the most common means of mixing the two phases. The liquid ion exchanger (solvent) is in general dissolved in a carrier such as kerosene.

The phosphate esters seem to have received the most attention as solvents; of these, di-2-ethylhexyl phosphoric acid (HDEHP) has been studied the most thoroughly. The use of this reagent has increased greatly in recent years (Weaver, 1968) both in analytical procedures and commercially. For example, it has been used for recovering large quantities of fission-product RE's from nuclear reactor wastes, and as will be described later on an industrial scale by Molybdenum Corporation of America (Molycorp) in the processing of bastnaesite.

The long-chain amines and their salts have been evaluated as extractants for the RE's. Bauer (1966) reported that fractionation of two pairs of adjacent RE elements (lanthanum-berberium and thulium-sterbium) from a nitrate solution was feasible, but that high concentrations of lithium nitrate were required to obtain effective extraction, and that separation was markedly dependent on the addition of a chelating agent to the aqueous phase. Some of the quaternary ammonium compounds also are useful extractants, but neither these materials nor the amines appear to have yet reached large-scale utilization.

Naphthenic acids are among the newest extractants being examined for extraction and separation of the RE's. These acids have the general formula  $RCOOH$ , where R is a carbon derived predominantly from cyclopentane or one of its homologs, and are obtained as by-products in petroleum processing. Bauer and Lindstrom (1964) evaluated a naphthenic acid solvent for extraction of RE sulfates. The acid was an effective extractant for the RE elements when diluted with diethyl ether or n-hexanol, but gave only moderate separation of the elements. The addition of chelating agents markedly improved the separation factors.

A major advantage cited for the solvent extraction method is that it can be made a continuous process, so that large quantities of product can be made in comparatively small plants. A disadvantage is that the process is inflexible and cannot easily be changed from one product to another.

Liquid ion exchange by centrifugal contacting has been reported recently (Chem. Eng. News, Mar. 11, 1968) as being used by Denison Mines in its rare earth recovery unit operated in conjunction with uranium production facilities at Elliot Lake, Ontario. The contactors, Podbielniak Pods manufactured by Baker Perkins, Inc., are said to give the same results as a series of mixer-settler tanks, conserving valuable plant space and sharply reducing the inventory of organic solvent (for example, from 75,000 gallons to 3,000 gallons).

6. *Potential new separation techniques.* Two literature disclosures have been noted which may be of future interest for effecting separations of the rare earths. Eisenbraut and Siever (1965) have described volatile rare earth chelates made from 2, 2, 6, 6-tetramethyl-3, 5-heptanedione (dipivaloylmethane). These rare earth complexes were thermally stable and showed appreciable and significant differences in volatilities based on sublimation and gas chromatographic data.

A new organouranium compound, bis-cyclooctatetraenyl-uranium, called "uranocene" on the basis of its similarity in structure to ferrocene, was recently synthesized at the University of California (Chem. Eng. News, Jan. 6, 1969). This compound is said to be the only one made and identified to date in which the pi-molecular orbitals of a large organic ring share electrons with the uranium f-atomic orbitals. It is suggested that the rare earths, because of their electronic structure, may enter into a comparable type of f-orbital union with large organic ring systems.

Uranocene is a green crystalline material which is pyrophoric but thermally stable in the absence of air. It is sparingly soluble in organic solvents and stable to water, acetic acid, and aqueous caustic soda. The material has a high volatility compared with other uranium derivatives, subliming at 180° C and 0.03 torr.

Ferrocene, bis-cyclopentadienyliron, was first synthesized in 1951, and is now used in a variety of applications from antiknock additives to polymerization catalysts. The sandwich structure of the new uranium derivative compared with ferrocene is shown in figure 2.

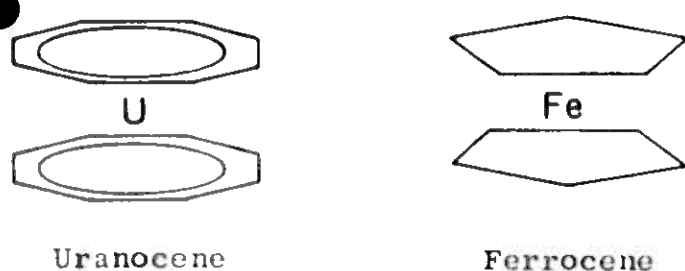


FIGURE 2—Sandwich structures of uranocene and ferrocene.

Extraction chromatography is a very new technique in which one of the liquid phases is held stationary on a columnar supporting medium. Either the aqueous phase or the organic extractant may be the stationary phase, but best results apparently are obtained with the organic phase stationary (Weaver, 1968).

Finely divided inert organic materials such as cellulose powder, polyethylene, Teflon, Kel-F, etc., are widely used. Inorganic powders such as kieselguhr, diatomaceous earth, and silica gel made hydrophobic by an adherent film of dimethyl dichlorosilane or a similar material also are useful. Extraction-chromatographic columns may be prepared by mixing the support material with an extractant and loading the mixture into a column, or by pouring the extractant into a column of supporting material, followed by flushing out of the excess with an aqueous solution. The result is a multi-stage unidirectional extraction column. When an extractant is the stationary phase, the elements to be separated are loaded on the column in an aqueous solution from which they are readily extractable and are then selectively stripped or eluted by a suitable aqueous phase. The similarity of such columns to ion exchange is at once apparent.

The technique has been developed into a useful tool for analysis of mechanisms of extraction, but it is doubtful that it will ever be useful for the separation of any considerable quantities of natural RE's. Capacities of the columns are considerably less than those of solid ion exchange columns

of the same size, and an extremely large scale-up would be required for processing useful quantities of RE's. The technique is not likely to become competitive with other separation methods, but will probably find increasing use in the separation of radioactive elements.

## PLANT PROCESS

The following description covers the processing of bastnaesite, currently the major source of rare earths. Process descriptions have been given by Chem Eng., Nov. 20, 1967; N. L. Johnson (1966); H. W. Harrah (1967); P. R. Kruesi and George Duker (1965); F. M. Lever and J. B. Payne (1968); and V. E. Shaw (1959).

The Mountain Pass, California, mine and processing plant has been developed and expanded by MolyCorp into the largest rare earth concentrating facility in the world. The principal mineral is bastnaesite, a fluorocarbonate containing chiefly cerium, lanthanum, neodymium, and praseodymium, but also small amounts of samarium, gadolinium, and europium. After open-pit mining, crushing, and grinding, the ore is subjected to hot froth flotation to give a concentrate averaging 60 percent REO. Careful control of pH and of reagents is necessary in the flotation.

Some of the concentrate is shipped without further treatment; some is subjected to acid leaching which further concentrates the mineral to 70 percent REO, and finally to calcination which gives a 90 percent REO concentrate for feed to the solvent extraction circuit.

The roasted concentrate is leached with hydrochloric acid for conversion to rare earth chlorides. The acid slurry is passed through a counter-current decantation and thickening circuit, then filtered to give a filter cake consisting of 65-70 percent REO containing 55-60 percent of cerium oxide. This precipitate is repulped, filtered, dried, and marketed as a cerium concentrate.

The thickener overflow contains 100 grams per liter of REO, including 0.2 gpl of europium. This solution is filtered, the pH adjusted to 1, the solution heated to 140° F, again clarified by filtration, and fed to the europium extraction circuit. The europium solvent extraction process was largely developed in 1961-1965 during laboratory and pilot plant work carried out for MolyCorp at the Colorado School of Mines Research Foundation, Inc. The process leads to europium oxide of 99.9 percent purity, together with by-products including samarium and gadolinium (Chem. Eng., Jan. 2 and Nov. 20, 1967; Jour. Metals, Aug., 1965).

The solvent extraction (liquid ion exchange) is carried out in mixer-settler units, using a volume ratio of 1.2 organic to 1.0 aqueous, the organic phase comprising 10 percent di-2-ethylhexyl phosphoric acid (HDEHP) in kerosene. The organic phase, which contains europium, samarium, and gadolinium, is stripped with 4N hydrochloric acid. Iron is removed from the hydrochloric acid strip solution by precipitation at a pH 3-3.5, then the solution re-extracted with the same solvent, and the organic phase stripped with 5N hydrochloric acid at a volume ratio of 8 organic to 1 aqueous. Samarium and gadolinium are recovered from the strip solution as carbonates, and europium oxide prepared for market.

The raffinate from the europium extraction is used as feed to a lanthanum recovery circuit, the first step being addition of ammonia and sodium hydrosulfide to precipitate

lead as the sulfide. The filtrate is clarified by filtration, then ammonia added to precipitate lanthanum hydrate which is filtered and dried.

The Mountain Pass facilities, together with the Molycorp plant at Louviers, Colorado, are stated to have the following capacities in pounds per year (J. G. Cannon, 1969): cerium concentrate 15 million, lanthanum-neodymium-praseodymium concentrate 12 million, samarium-gadolinium concentrate 240,000, lanthanum oxide 700,000, neodymium oxide 200,000, yttrium oxide 100,000, samarium oxide 150,000, praseodymium oxide 60,000, gadolinium oxide 50,000, and europium oxide 20,000.

The Research Foundation played an important part by providing the initial yttrium concentrate raw material for Molycorp's Louviers plant. Over 200,000 pounds of yttrium oxide equivalent was prepared in the Foundation's chemical pilot plant, and the availability of this material made possible an early start-up of the Louviers facility, which began commercial production late in 1966 (Chem. Eng. News, Jan. 2, 1967).

### PREPARATION OF METALS

(See Block and Campbell, 1961; Carlson and Schmidt, 1961; Daane, 1961; Gschneider, 1964, 1968; Henrie and Morrice, 1966; Hirschhorn, 1968; Hopkins, 1939; Kleber and Love, 1963; Lever and Payne, 1968; Moriarty, Jr., 1968; Morrice and Henrie, 1967; Morrice and Knickerbocker, 1961; Morrice and others, 1968.)

Production of the rare earth metals in high purity has proved very difficult. Reduction of rare earth compounds to the metal is not easy, and the produced metal is very reactive in the molten state so that contamination is difficult to avoid. Many of the metals have very high melting points, so that the reactions must be carried out in high vacuum or in an inert atmosphere; finding nonreactive materials of construction to contain the hot metals becomes a problem. Above 1,500° C the most useful materials appear to be tantalum, tungsten, and sintered beryllium oxide. Daane (1966) points out that the metal-oxygen bond in the rare earth oxides is one of the most stable bonds known, and the difficulty in preparing most of the rare earth metals from their oxides is related to this stability and to the high melting points of the oxides that inhibit chemical reactions.

Accordingly, the rare earth metals have most generally been prepared by first converting the oxides to the halides which have much lower melting points and are much more conveniently reduced by another active metal, or electrolyzed to form the metal. Historically, yttrium was first produced in 1825 and cerium in 1827 by reduction of the chlorides with sodium or potassium; lanthanum and cerium were prepared in 1875 by electrolysis of the fused chlorides. These two basic methods, metallothermic reduction and electrolysis of fused salt mixtures, have remained the principal methods of metal preparation.

In general, the anhydrous chlorides, bromides, and iodides of the rare earths are very hygroscopic, and the fluorides are easier to work with, although it has been found difficult to remove the last traces of oxygen from the fluorides. Mischmetal, cerium, and lanthanum are manufactured commercially by electrolysis of fused chloride baths containing alkali- and alkaline-earth chlorides. Hirschhorn (1968) points out that metals of high purity (99.9 percent) can be

produced by fused salt (chloride) electrolysis if carefully purified feed materials are used and if cell atmosphere composition is controlled. A recent development is chlorination of monazite or bastnasite to produce an anhydrous rare earth chloride suitable for electrolysis without further processing. (See also Brugger and Greinacher, 1967.) As a generality, production of extremely high purity metals by electrolysis is hard to achieve, because of almost inevitable contamination from the electrolyte and cell material. Commercial cells have been constructed of iron, graphite, and ceramic.

Yttrium and the heavy earths cannot be produced as massive metals from fused chloride electrolytes because their melting points are well above the temperature of the fused electrolyte. Under these conditions the metal is formed as a powder in the electrolyte, making separation of the clean metal very difficult. Henrie and Morrice (1966), Morrice and Henrie (1967), and Morrice and others (1968) were able to obtain massive gadolinium, yttrium, and dysprosium by electrolysis of the oxide dissolved in a fluoride bath (for example, RE fluoride plus lithium fluoride) at temperatures up to 1,700° C. High purity neodymium, praseodymium, dysprosium, cerium, lanthanum, dysprosium, gadolinium, and yttrium, as well as a number of alloys were prepared by this method. In general, however, the higher melting rare earths have been prepared by metallothermic reduction rather than by electrolysis.

As mentioned above, the fluorides of the rare earths offer certain advantages over the chlorides in ease of preparation from the oxides, stability in air, and quantitative reduction to metal. Four general methods are used to prepare the fluorides. These are:

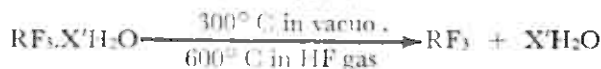
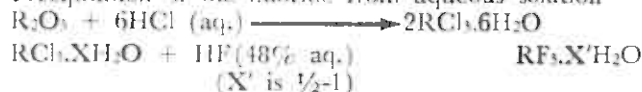
1. Direct reaction of the oxide with anhydrous HF



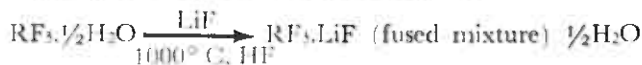
2. Reaction of the oxide with ammonium bifluoride



3. Precipitation of the fluoride from aqueous solution

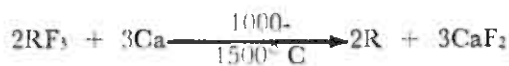


4. Passage of anhydrous HF through a molten fluoride salt, which is essentially a purification method



Methods (3) and (4) were used by Lunex Company (Moriarty, 1968), but it was found that the fluorides could not be satisfactorily dehydrated for industrial scale operations because of the formation of oxyfluorides.

Reduction of the fluoride to the metal can be carried out with calcium:



Both the rare earth metal and the calcium fluoride are liquid at this temperature and insoluble in each other.

The calcium reduction method cannot be used for the preparation of samarium, europium, or ytterbium; trihalides of these rare earths give only the dihalide and no metal. It is possible to reduce the oxides of these metals by heating with about a 10 percent excess of lanthanum metal at about 1,000° C. Lanthanum oxide is formed and the volatile RE metal distills and condenses on the upper part of the crucible.



Some properties of the oxides and of the RE metals are given in table 5 (Gschneider, 1968).

TABLE 5.—Properties of rare earth oxides and metals

| Metal        | Melting point ° C | Vickers hardness kg/mm <sup>2</sup> | Oxide                           | Melting point ° C |
|--------------|-------------------|-------------------------------------|---------------------------------|-------------------|
| Yttrium      | 1526±5            | 38                                  | Y <sub>2</sub> O <sub>3</sub>   | 2415              |
| Lanthanum    | 920±1             | 37                                  | La <sub>2</sub> O <sub>3</sub>  | 2250              |
| Cerium       | 798±3             | 24                                  | Ce <sub>2</sub> O <sub>3</sub>  | 2140              |
|              |                   |                                     | CeO <sub>2</sub>                | 2400              |
| Praseodymium | 931±4             | 37                                  | Pr <sub>2</sub> O <sub>3</sub>  | 2200              |
|              |                   |                                     | Pr <sub>6</sub> O <sub>11</sub> | 2040              |
| Neodymium    | 1016±5            | 35                                  | Nd <sub>2</sub> O <sub>3</sub>  | 2272              |
| Promethium   | 1080±10           | —                                   | —                               | —                 |
| Samarium     | 1073±1            | 45                                  | Sm <sub>2</sub> O <sub>3</sub>  | 2325              |
| Europium     | 822±5             | 17                                  | EuO                             | 1950              |
|              |                   |                                     | Eu <sub>2</sub> O <sub>3</sub>  | 2050              |
| Gadolinium   | 1312±2            | 57                                  | Gd <sub>2</sub> O <sub>3</sub>  | 2340              |
| Terbium      | 1357±6            | 46                                  | Tb <sub>2</sub> O <sub>3</sub>  | 2387              |
| Dysprosium   | 1409              | 42                                  | Dy <sub>2</sub> O <sub>3</sub>  | 2340              |
| Holmium      | 1470              | 42                                  | Ho <sub>2</sub> O <sub>3</sub>  | 2405              |
| Erbium       | 1522              | 44                                  | Er <sub>2</sub> O <sub>3</sub>  | 2390              |
| Thulium      | 1545±15           | 48                                  | Tm <sub>2</sub> O <sub>3</sub>  | 2400              |
| Ytterbium    | 816±2             | 21                                  | Yb <sub>2</sub> O <sub>3</sub>  | 2346              |
| Lutetium     | 1663±12           | 77                                  | Lu <sub>2</sub> O <sub>3</sub>  | 2490              |

#### USES OF RARE EARTHS AND RARE EARTH COMPOUNDS

The rapid growth of literature relating to the rare earths is nowhere better shown than in the area of new and proposed uses for these materials. For example, Mandle and Mandle in their 1964 chapter on "Uses and Applications" list 837 references, none of which discloses any application in lasers; in their 1966 chapter, 1,090 new references are listed, 148 of which relate to lasers. It is apparent that a great deal of research has been done and is continuing, to find new outlets for the rare earths as they become increasingly available at lower prices and in increasingly higher purity.

Mischmetal has been made commercially since the early 1900's, and cerium, lanthanum, and didymium metals (electrolytic) have been marketed since the 1940's. The

high-purity rare earth and yttrium metals became available on a commercial scale in the late 1950's. Until a very few years ago the standard use-distribution pattern showed about one-fourth of the materials going into alloys (mischmetal), used in lighter flints, magnesium alloys and some ferrous alloys. Another one-fourth was used in the glass industry, for coloring and decolorizing, and the cerium oxides were widely used in polishing. The third one-fourth of rare earth production went into the manufacture of carbon arc electrodes, used in the motion picture industry and in large searchlights. The remaining one-fourth was divided among many miscellaneous uses.

In contrast with the above distribution, the figures given by Parker (1967) for 1967 show that of the \$15 million total sales of RE materials, about 50 percent was accounted for by shipments of europium and yttrium oxides of high purity (for use in TV tubes, mercury vapor lamps, and fluorescent lighting fixtures), although these materials made up only one percent of the total weight of RE materials. The industrial consumption of other rare earth compounds on the basis of value is given as follows:

|                                                                               | Percent |
|-------------------------------------------------------------------------------|---------|
| Glass, usually as polishing powders, and some in ceramics and glazes          | 17      |
| Petroleum catalysts                                                           | 10      |
| Steel and alloy production and in the making of mischmetal and lighter flints | 5       |
| Carbon arc production                                                         | 5       |
| Electronics                                                                   | 5       |
| Other miscellaneous applications                                              | 8       |
|                                                                               | 50      |
| High purity europium and yttrium oxides                                       | 50      |
|                                                                               | 100     |

Kruesi (1968) states that the principal use for the rare earths in terms of pounds has become that of petroleum catalytic cracking, which is seen to account for 10 percent of the annual value of the RE compounds.

The following table from Gschneider (1968) gives figures for volume and for dollars for the rare earths in 1966.

TABLE 6.—Rare earths consumed in 1966

| Million lbs/year | %    | Million \$/year | %    | Application                |
|------------------|------|-----------------|------|----------------------------|
| 2.1              | 26.2 | 0.4             | 2.6  | Metallurgy                 |
| 2.0              | 25.0 | 1.95            | 12.9 | Glass polishing            |
| 1.45             | 18.1 | 0.5             | 3.3  | Catalysts                  |
| 0.7              | 8.8  | 0.8             | 5.3  | Carbon arcs                |
| 0.6              | 7.5  | 0.5             | 3.3  | Research and miscellaneous |
| 0.5              | 6.2  | 0.75            | 5.0  | Glass and ceramics         |
| 0.35             | 4.4  | 9.7             | 64.2 | Phosphors                  |
| 0.25             | 3.1  | 0.2             | 1.3  | Capacitors                 |
| 0.05             | 0.6  | 0.3             | 2.0  | Microwave                  |
| 8.00             | 99.9 | 15.1            | 99.9 |                            |

A list of some of the applications of the rare earths is given in the following table, also from Gschneider (1968). Some of the present and proposed applications will be discussed in greater detail following.

TABLE 7.—Applications of the rare earths\*

| METALLURGY                           | GLASS                 |
|--------------------------------------|-----------------------|
| Alloying agent                       | Polishing—I, M        |
| Ferrous—M                            | Decolorizing—I, M     |
| Magnesium—M, I                       | Coloring agent—I      |
| Other—M                              | Filters—I             |
| Pyrophoric alloys—M, I               | Optical glass—I       |
| Pure metals for research—I           | Photochromic glass—I  |
| CERAMICS                             | ELECTRONICS           |
| Enamels and glazes—I, M              | Capacitors—I          |
| Coatings—M, I                        | Cathodes—I, M         |
| Refractories—I                       | Computer components—I |
| Stabilizers—I, M                     | Electrodes—I, M       |
| ILLUMINATION                         | Garnets—I             |
| Carbon arc—M                         | Getters—M, I          |
| Lasers—I                             | Ferrites—I            |
| Phosphors—I, M                       | Insulators—I, M       |
| Fluorescent lamps—I                  | Magnets—I, M          |
| Mercury vapor lamps—I                | Resistors—I           |
| Color television—I                   | Semiconductors—I      |
| NUCLEAR                              | Thermistors—I         |
| Control rods—I                       | MISCELLANEOUS         |
| Burnable poisons—I                   | Catalyst—I, M         |
| Diluents—I                           | Pharmaceuticals—I     |
| Shielding—I                          | Photography—I         |
| Detectors—I                          | Analytical—I          |
| Radioactive heat and power sources—I | Lubricant—I           |
| Counters—I                           | Chemical processing—I |
|                                      | Thermometers—I        |

\*The letter M after an application indicates that the rare earths are used as a mixture and the letter I indicates that individual rare earths are used. If both letters are given it indicates that both forms are used; the first letter indicates that the utilization is greater in that form than it is the other.

On a volume basis the applications using the mixed, unseparated rare earths account for 80 percent of the domestic production, but on a dollar basis this accounts for only about 25 percent of the total amount spent. In other words, the market for the separated individual elements accounts for only 20 percent of the total volume of rare earths produced, but 75 percent of the total dollar value.

**Phosphors.** One of the most important uses for the rare earths that has developed in recent years is in color television tubes; the use of europium and yttrium oxides as phosphors is now well established. In this application, europium-activated yttrium vanadate, yttrium oxide, or yttrium oxysulfide as the red phosphor gives brighter, truer colors, and improves the quality of the picture. The previously used silver-activated zinc cadmium sulfide red phosphor did not have a high enough luminosity to match the green and blue colors, so that the greens and blues were deliberately deadened to

obtain a good color balance with the red. The new RE phosphor allows full brightness of the green and blue phosphors, thus resulting in a 40 percent gain in overall tube brightness.

Closely allied to this use is the use of a glass filter plate containing neodymium oxide, which when laminated onto the viewing surface of color TV tubes reportedly improves the brightness and contrast and produces more saturated red, green, and blue colors. Phosphors containing europium and yttrium also are used in improved fluorescent lamps, and industrial mercury vapor lamps are improved by an addition of dysprosium (Parker, 1967). As noted above, these outlets amounted to over \$7 million in 1967, accounting for about half of the total dollar value of the RE industry.

**Cracking catalysts.** Another very recent and important application of the rare earths is in the preparation of catalysts for cracking of petroleum. This use is now the largest single volume outlet for these materials and accounted for about 10 percent of the dollar value in 1967. Mandle (1966) has summarized the various literature references dealing with these new superactive, superselective catalysts, which are classified as "metal-acid aluminosilicates," being closely related to the well-known zeolites or molecular sieves. The commercial cracking catalyst is called Durabead 5. Tests of the new catalyst showed that 1/16th as much catalyst gave more conversion than a conventional silica-alumina catalyst in 1/16th the time of contact, leading to the claim that the RE catalyst is more than 100 times as active. It is said that the economic significance of this development in gasoline production is tremendous, since it yields 18 to 20 percent more gasoline from a given amount of charge stock, at the expense of components of less value, and has decreased regeneration requirements.

Reportedly the improvements resulting from the use of this catalyst are so remarkable that it has been necessary to redesign the distillation processes associated with the cat cracker in the refinery. Two major advantages of the zeolite-type catalysts over amorphous catalysts are claimed:

- (1) In the zeolites the catalyst metals appear to be distributed as atomic particles, rather than as metal crystals, and are, therefore, more active.
- (2) According to the patents, the catalytic metals expose up to four times as much surface in the zeolites as they do in amorphous catalysts.

In the Durabead 5 catalyst, rare earth ions displace some of the sodium ions of the supporting synthetic zeolite structure. These RE ions are introduced by an ion exchange process from a chloride solution, to give an RE content in the catalyst of about 5 percent, as the oxide. The RE is a mixture of the lower atomic weight members, such as lanthanum, cerium, praseodymium, neodymium, and samarium (Chem. Eng. News, May 10, 1965).

Other catalytic applications of the rare earths have been known for many years, and research in this area is continuing.

**Lasers.** By far the most exciting of the newer applications of the rare earths is in lasers, so much so that it is difficult to avoid superlatives when discussing this new field of activity. Lasers were first proposed in 1958 and the first working laser was made in 1960. Since then there has been an unprecedented amount of activity involving this new kind of light source; in the 18 months following the first laser about

400 companies entered into work with the device and many government agencies adopted some sort of laser program (Lengyel, 1962).

Levine (1963) notes that very few developments have stimulated the imagination of scientists and engineers as has the laser—it is now one of the major research undertakings in the United States and its growth is probably unparalleled in the history of science and technology. The amount of research and advanced engineering devoted to lasers exceeds that devoted to transistors at a comparable stage of development. It is estimated (Chem. Week, Apr. 23, 1966) that as much as \$1 billion will be spent on laser materials and equipment in 1970.

The rare earths are particularly suitable for this specific application on the basis of their atomic structure, crystal formation, and optical and spectral properties. So far the amounts of materials involved are relatively small, and it must be emphasized that the rare earths are used in only a part of the many lasers which have been developed. However, the possibilities in this area appear to be so tremendous that the subject justifies more than passing mention.

Basically a laser is a totally new kind of light source, involving a special form of luminescence, in which a highly parallel, intense beam of coherent radiation is emitted. This unusual source of light can be made brighter than the sun, and man's control of light has thus reached an entirely new level. It is this element of control which excites workers in the field with prospects of totally new uses for light that are as yet unknown. The term laser is an acronym for light amplification by stimulated emission of radiation and is an outgrowth of the earlier maser (in for microwaves). The laser is also termed an optical maser. Light amplification has been achieved with gases, liquids, and solids, involving many different molecules and a variety of ways of exciting them. The rare earths have been used in solids and in liquids.

Essentially, laser action involves stimulation of an active material by an external source to raise part of the atoms to a higher energy level (excited state) than the normal ground level. The excited atoms may then return spontaneously to the ground state, emitting energy, or, if stimulated while in the excited state will emit energy which is in phase with and in addition to the stimulating radiation—this is stimulated emission, and the highly parallel, intense beam of coherent radiation has many important applications. Some of the major present and potential uses of lasers are shown in the tabulation following.

- (1) Communications. Moving from microwave to the visible-light band of frequencies expands the available band by a large factor (over 10,000) so that the laser could accommodate 80,000,000 TV channels of the present bandwidth, or 800,000,000 simultaneous telephone conversations. The laser beams are of particular importance for communications in space, where the atmosphere does not interfere with the propagation of radiation.
- (2) Concentration of power. It is possible to focus a laser beam to a very small point to achieve intense heating, reaching a power of 10,000 times greater than the sun under certain conditions. Even the most refractory materials can be melted or vaporized under these conditions. This aspect of the laser has been used in welding and in certain types of surgery, for example, for repair of a detached retina, and it obviously has military implications. The laser provides an unusual tool for the

study of interaction of matter with radiation of extremely high density.

- (3) Scientific experimentation. Range finding, or "ranging," the determination of the position of a distant object by laser is similar to radar. The laser offers possibilities in modification or acceleration of photochemical reactions, and in biological applications; for example, stimulating growth or destroying certain tissues. The laser offers an intense source of monochromatic radiation in the visible, the infrared, and the near ultraviolet, that can be focused to a fine point.

The rare earth elements have very complex spectra due to electronic transitions between various electronic levels. Since each element has its own electronic level scheme, there are numerous transitions which make the elements useful as phosphors and laser materials. Practically all of the rare earths have been evaluated in lasers: as crystals, in glasses, in chelates (organic compounds), and in liquids. Gschneider (1968) notes that neodymium is one of today's most useful laser materials, and that yttrium oxide and other yttrium compounds are becoming the most important host materials for rare earth dopants (activators) for either phosphor or laser action. Thus, a neodymium-doped yttrium aluminum garnet (YAG) is one of the most promising laser developments, and a holmium-doped erbium oxide has been evaluated. In these newer approaches to laser crystals, the host materials include RE (or related) elements that can aid in the excitation of the active dopant ions—this allows easy, low-threshold pumping, that is, excitation (Chem. Week, Apr. 23, 1966).

Parker (1967) reports that yttrium aluminum garnets doped with neodymium oxide were used in a sun-pumped laser capable of carrying television modulation. Neodymium glass lasers showed promise in microwelding applications. Hydrogen-free solvents, containing RE oxides such as neodymia in solution, were believed to be at least as efficient as some of the crystalline lasers and have the advantage that the liquid can be cooled by circulation.

The field of laser technology appears to have an almost unlimited potential for further growth and development. Because of the particular characteristics of the rare earths which make them of value for this application, it seems certain that the rare earth industry will benefit from any large scale commercialization in this area.

*Glass and ceramics.* (See Mandle and Mandle, 1964; 1966; Gschneider, 1968; Herring and others, 1968; Parker, 1967; Chem. Eng. News, May 10, 1965, June 12, 1967; Chem. Eng., Jan. 2, 1967; Chem. Week, Dec. 2, 1967; Cannon, 1969). The glass and ceramics industries still rank as major outlets for rare earth products, based on both dollar value and pounds. The largest consumption in this field appears to be for glass polishing, based chiefly on cerium oxide or high-cerium mixtures. Thus, some of the polishes contain 90 percent cerium oxide, although most are mixtures of RE oxides in about the same proportions as they occur in the ore; for example, 50 percent cerium oxide and 24 percent lanthanum oxide, with smaller amounts of other RE oxides. A process has been patented for making a high speed glass polishing powder directly from bastnaesite.

The RE oxide polishing powders are used in the polishing of plate glass, mirrors, television tubes, spectacle lenses, camera and instrument lenses, etc. In general, they are much cleaner and faster than the traditional rouge, produce a superior finish, and have a longer useful life. Accordingly,

these RE materials are competitive with rouge even though their cost may be ten times greater. There is some question as to whether use will continue to increase in the large volume outlet for polishing plate glass because of the introduction of the float glass (Pilkington) process which eliminates most of the polishing.

Another large potential outlet for the RE's in glass is in the use of cerium and neodymium oxides in the glass batch for decolorizing. This combination is said to be competitive with the selenium-cobalt system commonly used today, and a market equivalent to 2 million pounds of cerium oxide annually is anticipated. The use of cerium for decolorizing requires an arsenic-free glass batch, since arsenic-cerium glasses are photosensitive and develop a brown color when exposed to sunlight.

Several of the rare earths have found use in the making of special optical glasses. Lanthanum oxide has been used in ophthalmic glasses and in special glasses used in photographic lenses. Cerium dioxide is used in glasses which are subject to discoloration by various kinds of radiation (alpha, gamma, x-ray, light, electron), the effect apparently being due to the strong oxidizing power of the  $Ce^{+4}$  ion, which prevents lower-valence lead and iron compounds from forming. This feature is useful in glass for cathode-ray tubes, apparatus used near nuclear reactors, and in color TV tubes, where electron radiation could cause the glass to discolor and destroy the color quality of the picture. Cerium oxide in glass also absorbs ultraviolet and prevents spoilage of food in transparent containers; cerium, neodymium, or didymium (neodymium plus praseodymium) oxides are used to absorb ultraviolet radiation in welder's and glass blower's goggles, sunglasses, optical filters, etc.

Samarium and erbium have been used in special luminescent and infrared-absorbing glasses, and neodymium and praseodymium also accentuate infrared absorption.

Several of the rare earths give interesting colors in glasses. Neodymium has enjoyed the widest use of any of the RE's as a glass colorant: it gives beautiful tones ranging from blue (under fluorescent light) to wine red (in natural daylight or incandescent light), and is said to produce the only known glass with a bright purple color. Mixtures of neodymium and praseodymium give unique glasses in which the color varies with the thickness of the glass and with the kind of illumination. Glasses containing praseodymium are green, the color being essentially the same as that of chromium-containing glasses, although their absorption spectra are quite different. Erbium glasses are pink, and represent the only truly stable, pink, soda-lime glasses, and a mixture of erbium and neodymium gives a pleasing lavender color. Research is said to be in progress on developing photochromic glasses, that is those that darken in the presence of light (certain wavelengths) and lose their color when the light is removed. Europium has been disclosed as sunlight-sensitive, and cerium and other RE's are used for exposure to other light sources.

A number of the rare earths also yield fluorescent glasses, europium having received considerable attention, probably because of its striking orange-red color. Dysprosium produces a yellow fluorescence, and cerium or thulium gives blue; essentially any fluorescent color can be obtained by using mixtures of the various rare earths. The rare earth fluorescent glasses have been suggested as standards for fluorescence spectrophotometry.

In the field of ceramics, a mixture of praseodymium oxide

with zirconium oxide produces a pure yellow that is used in coloring ceramic tile and porcelain enamel. A new polycrystalline material which comprises a solid solution of 90 percent yttrium oxide and 10 percent thorium oxide, called Yttralox (General Electric Co.) is transparent and melts at a temperature of 1,000° F, compared with a softening range of 2,000-2,600° F for typical glasses. It is being considered for use in high intensity incandescent and discharge lamps, in windows of high-temperature furnaces, and in microscope lenses used to study molten samples. The material is said to be transparent to visible and to infrared light, and to be amenable to fabrication by ceramic-processing techniques.

Yttrium and cerium oxides are used in stabilizing zirconium dioxide in certain applications. The rare earth oxides have high melting points, but are reactive at high temperatures and tend to form compounds or solid solutions with other oxides, and do not appear to offer any outstanding benefits over the more common oxides as refractories. Holmium oxide reportedly has been used as a special refractory.

**Metallurgy.** Many references have been published on the use of rare earths in metallurgy, particularly ferrous metallurgy, starting with mischmetal in the early 1900's. Much of this work was and has continued to be based on mischmetal, which was the first of the RE metals to be produced commercially and which has been available at a much lower price than any of the separated rare earths. The field of ferrous metallurgy appears to offer the largest potential outlet for the rare earths, because it is the largest market in metallurgy and because some of the early work in this area indicated considerable promise. However, none of the hoped-for large scale applications in ferrous metallurgy have yet materialized. Mandile and Mandile (1964) point out that in the early 1950's rare earth additions in the steel casting industry were glowingly described as "wonder drugs," and "the penicillin of steel," and that in some cases the titles were merited, although many contradictory results were obtained.

Plain carbon and low alloy steels represent by far the largest tonnage of metal produced throughout the world. Rare earth additions to these steels have been shown to be useful in deoxidation, desulfurization, and in improvement of physical properties such as ductility and impact resistance, and this is still the field of greatest research effort as indicated by the technical literature. Several factors appear to be responsible for the lack of greater use in steels (Mandile and Mandile, 1966):

- (1) Economics presently does not favor use of the RE metals or salts compared with other products; for example, aluminum for deoxidizing. Except in special cases, the RE's are too expensive for removing sulfur from steel.
- (2) The introduction of the RE's in the manufacturing process is not easy; for example, the effectiveness of the RE addition can be influenced by the type of refractory used.
- (3) There is considerable loss of RE to the slag, and this loss varies markedly with a slight change in conditions. This erratic loss of the RE's during processing probably is responsible for much of the controversy as to the actual benefits of RE additions.
- (4) The exact amount of RE addition needed to give best results is not yet established, and the exact process details have not been developed. This is probably the most important factor.

In stainless steels also, there appears to have been considerable divergence of opinion as to the merits of RE addi-

tions, but this field too continues to be of interest, particularly in Russia.

Ductile iron (nodular iron) represents one of the important metallurgical applications for mischmetal. This iron shows high strength and ductility, good corrosion resistance (at least equal to gray iron), and good machinability, and more nearly resembles steel than gray iron. Magnesium is used in production of most of the ductile iron, and mischmetal or cerium additions are said to reduce the effect of subversive elements (titanium, lead, bismuth, antimony, arsenic, aluminum, etc.), help desulfurization, increase magnesium recovery, and increase ladle fluidity. Additions of the RE may be made separately following the magnesium addition, or as a silicon-magnesium-mischmetal alloy or other alloy. Kanter and others (1962) have suggested the addition of yttrium to cast iron, citing advantages over the widely used magnesium and over cerium, but there does not appear to have been any commercial use of this RE, possibly based on cost considerations.

Many alloys of the rare earths have been described in the literature, the most important being that of the RE's with each other, mischmetal, with a typical composition of 45-50 percent cerium, 22-25 percent lanthanum, 15-17 percent neodymium, 8-10 percent other rare earths, up to 5 percent iron, 0.1-3 percent silicon, and smaller amounts of calcium, magnesium, aluminum, oxygen, nitrogen, and carbon. The oldest, and still one of the most important uses of mischmetal is in the manufacture of sparking metal alloys for cigarette lighter flints and welding gas igniters. These pyrophoric alloys contain 70 to 80 percent of mischmetal and 20 to 30 percent of iron.

Mischmetal is added to magnesium and aluminum alloys to provide strength at high temperature; for example, in aircraft frames and in aluminum pistons for internal combustion engines. In recent years there has been some replacement of the RE's in magnesium alloys by thorium, and some evidence that didymium (praseodymium plus neodymium) is superior to cerium or to mischmetal in obtaining higher performance alloy castings. There is little activity evident at present in use of the RE's in aluminum alloys.

A great number of other alloys of the rare earths have been reported in the literature, none of which apparently has reached the stage of major commercial significance. As examples, yttrium additions of about 1 percent to chromium improve the oxidation resistance of high temperature service alloys due to improving adherence of the oxide coating to the surface of the chromium-base alloys. Yttrium additions also lower the ductile-brittle transition of chromium. Yttrium additions to molybdenum greatly increase the strength, hardness, and recrystallization temperature of molybdenum. Yttrium additions to niobium-base alloys improve the ductility, high temperature strength and fabricability, and reduce the oxygen and nitrogen contents, grain size and the degree of coring.

**Carbon arc electrodes.** Use of the rare earths in carbon arc electrodes dates back to the early 1900's, being one of the first major uses of rare earth compounds (fluorides plus oxides), and accounting for about one-fourth of the rare earth market for many years. The electrodes are made by forming the electrode as a hollow carbon tube which is filled with a mixture of RE fluoride and oxide to give a compromise between luminosity and speed of volatilization. The cored carbons are used by the motion picture and TV industry, both in studio lighting and in projection because the

quality closely matches that of natural sunlight. Army, Navy, and Coast Guard searchlights also use these RE cored carbons because of the high light output—the luminosity of the cored electrode is approximately ten times that of a plain carbon electrode. The increase in light output is caused by some of the atoms in the volatilized RE compound being raised to an "excited" state by exposure to the flow of electrons from the arc; upon return to the ground or stable state the excited atoms emit energy as light. This phenomenon is similar in some respects to the excitation mentioned previously in connection with lasers, but the arc light does not radiate as a reinforced, coherent wave.

**Nuclear applications.** (See Anderson, 1961; Mandl and Mandl, 1964, 1966; Gschneider, 1968; Parker, 1967; Kleber and Love, 1963.) The greater availability and generally decreasing costs of the rare earths make them of continuing interest for nuclear uses. A table of the neutron absorption cross sections of the rare earth metals shows that they range from gadolinium, with the highest absorption cross section for thermal neutrons of any natural element (40,000 barns), to cerium with only 0.7 barns. The most important present and potential uses for the RE's in the nuclear field are as follows:

- (1) Neutron-absorber applications, that is, control rods, burnable poisons, flux suppressors, and shielding. Europium, dysprosium, samarium, gadolinium, and possibly erbium and thulium, are of interest in control rods. Erbium, dysprosium, europium, gadolinium, and possibly lutetium are considered as burnable-poison materials. Holmium, dysprosium, and europium might be of use as flux suppressors. In a new development, RE oxides such as dysprosium and erbium were combined with hafnium oxide, which also has a high neutron cross section, to make RE pyrohafnates. This provides an inexpensive way of incorporating hafnium into control rods. New ceramic pellets made of aluminum and samarium oxides or aluminum and gadolinium oxides can be used as atomic fire extinguishers by inserting them rapidly into a reactor to absorb excess neutrons whenever the reactor approaches a dangerous operating level.
- (2) Diluents in oxide or oxide-cermet fuels. The oxides of yttrium, lanthanum, and cerium, because of their low nuclear cross sections are used as diluents and/or stabilizers in oxide-base nuclear fuels.
- (3) Hydrides. Yttrium hydride is of particular interest, because it contains a large number of hydrogen atoms per cubic centimeter, nearly equal to that of water ( $5.3 \times 10^{22}$  for  $YH_2$  compared to  $6.7 \times 10^{22}$  for  $H_2O$ ). Also,  $YH_2$  loses very little hydrogen up to  $1,200^\circ C$ , making it an attractive nuclear shield for high temperature operations, and suggesting its use as a moderator. Cerium is also of interest, as are alloys of cerium and yttrium with zirconium.
- (4) Structural metals or ingredients to modify structural alloys. Yttrium is used as a container material for liquid alloys, such as uranium- and thorium-eutectic alloys. For example, yttrium pipe can carry the 5 percent Cr-95 percent U eutectic with essentially no corrosion at  $1,000^\circ C$ . Use of some of the RE's and of yttrium as alloy modifiers for zirconium and niobium is under study.
- (5) Highly efficient radiation shields have been developed which contain layers of carbon and lead, dysprosium

and lead, gadolinium alone and mixed with lead and tungsten, and a final layer of lead or tungsten with depleted uranium.

**Electronic and magnetic applications.** (See Gschneider, 1968; Mandl and Mandl, 1964, 1966; Spedding and Daane, 1961). There are many literature references to the use of various rare earth and rare earth compounds in applications which can be grouped under the broad generic classification of electronic and magnetic uses. Some of these will be discussed briefly.

In electron tubes, the RE's have been used as "getters," electrodes, and cathode emitters. The magnetic ceramics (ferrites) containing RE's are of particular importance, on the basis of their use in microwave electronics; for example, in electronic computers, in microwave transmission (telephone and TV), and as radar transmitters. The two compositions which have received most attention are the yttrium-iron garnets (YIG) and the yttrium-aluminum garnets (YAG), but a number of other RE's have been evaluated as ferrite materials. In the field of electronic capacitors, the REO ceramics using cerium or lanthanum with barium titanate appear to be of commercial interest. The RE titanates and stannates are used in ceramic capacitors in electronic components for missile and aircraft applications.

The subject of thermoelectric power generation has been of considerable interest, and semiconductors appear to be favorable materials for thermoelectric devices. Many rare earth salts have been evaluated for this purpose. Gadolinium selenide has been offered commercially in thermoelectric generating equipment. This product has shown the highest efficiency in the direct conversion of heat to electricity; lanthanum, erbium, and ytterbium selenides and tellurides, and the sulfides of cerium and samarium also show similar properties. Some of the materials (for example, cerium and samarium sulfides) can be used at temperatures of 1,000° C. for direct conversion of heat to electricity.

The magnetic susceptibility and magnetic moments of the RE metals, especially the heavy members, gadolinium to thulium, are the highest of all the elements. For example, holmium and dysprosium have the highest known magnetic moments of any element (10.6 Bohr magnetons, compared with 2.2 for iron), and have been evaluated as pole pieces of a cryogenic magnet for focusing high energy electrons.

Another recent development is the RE-cobalt permanent magnet, which may become one of the more important types of permanent magnets. In making the magnets, the alloy is ground to micron size, placed in an external magnetic field to align the magnetic poles of the particles, then pressed together to give a finished magnet. These more powerful magnets may lead to smaller electric motors, hearing aids, computers, etc. However, some problems are said to remain with corrosion of the RE-cobalt alloys.

Strat (1967) points out that the cobalt-RE alloys of the R-Co<sub>2</sub> and RCo<sub>5</sub> types show the best magnetic characteristics, with the rare earth chosen from yttrium, cerium, praseodymium, neodymium, or samarium, and with SmCo<sub>5</sub> and mischmetal Co<sub>5</sub> having the best opportunities for commercialization.

**Miscellaneous uses.** Many references show the RE's or RE compounds as minor but essential components in a wide variety of applications. In the category "Diverse Applications," Mandl and Mandl (1964) show 38 references; the same authors in 1966 list an additional 104 references in this category, distributed as follows:

| Field of use                     | Number of references |
|----------------------------------|----------------------|
| Electrical                       | 19                   |
| Chemical                         | 11                   |
| Polymers                         | 10                   |
| Medicinal or pharmaceutical      | 8                    |
| Instrumentation                  | 12                   |
| Foundry cores for metal castings | 5                    |
| Metallurgy                       | 7                    |
| Oils and lubrication             | 5                    |
| Rubber                           | 3                    |
| Pigments                         | 3                    |
| Photography                      | 4                    |
| Space technology                 | 4                    |
| Soils                            | 3                    |
| Miscellaneous                    | 10                   |
|                                  | 104                  |

## SUPPLIERS

The following companies are listed (Parker, 1967) as being active in various aspects of the production and marketing of rare earth compounds and metals.

### *Monazite, bastnaesite, and other RE concentrates:*

- Carpro Research and Engineering, Inc., near Jacksonville, Fla.
- Climax Molybdenum Co., Climax, Colo.
- Humphreys Mining Co., Folliston, Charlton County, Ga.
- Michigan Chemical Corp., St. Louis, Mich.
- Molybdenum Corp. of America, Mountain Pass, Calif.

### *Compounds and metals (including high-purity oxides):*

- American Potash and Chemical Corp., Rare Earth Division, West Chicago, Ill.
- W. R. Grace and Co., Davison Chemical Division, Chattanooga, Tenn., and Pompton Plains, N. J.
- Michigan Chemical Corp., St. Louis, Mich.
- Molybdenum Corp. of America, Louviers, Colo., Mountain Pass, Calif., and Washington, Pa.
- Research Chemicals, Division of Nuclear Corp. of America, Phoenix, Ariz.
- Union Carbide Corp., Alloy, W. Va.

### *RE compounds, small producers:*

- Atomergic Chemetals Co., Division of Gallard-Schlesinger Chemical Mfg. Corp., Carle Place, N. Y.
- Transelco, Inc., Penn Yan, N. Y.

### *Mischmetal:*

- American Metallurgical Products Co., Inc., New Castle, Pa.
- Ronson Metals Corp., Newark, N. J.

### *Higher purity metals:*

- American Potash and Chemical Corp., Rare Earth Division, West Chicago, Ill.
- Atomergic Chemetals Co., Division of Gallard-Schlesinger Chemical Mfg. Corp., Carle Place, N. Y.
- Lunex Co., Pleasant Valley, Iowa.
- Michigan Chemical Corp., St. Louis, Mich.
- Ronson Metals Corp., Newark, N. J.

## PRICES

Prices of rare earth materials, both the high-purity elements and the lower cost mixtures, are showing the inevitable effects of increasing demand and greater availability. Thus, average costs of the RE's have been decreasing at a rate of about 10 percent per year in recent years.

Certain factors should be kept in mind in assessing the present and potential price structure of this market. More uses have been developed and the market outlook appears to be much better for the light group RE's than for the heavy elements (holmium, erbium, thulium, lutetium). Some of the RE's (europium, thulium, lutetium) are genuinely rare, and probably always will be expensive. For example, more than 10,000 pounds of RE ore must be processed to obtain one pound of europium oxide. The RE's usually all occur together and associated with yttrium, so that demand for one of the elements leads to concomitant production of the associated members. In such cases, the product desired must bear the major part of the cost of separation, and the other materials are accumulated as by-products. As a more balanced market is developed for the entire RE family, separation costs can be shared and prices should show a further decrease.

Some quoted prices (Parker, 1967) which appeared early in 1968 are given in the following tabulations, together with some up-to-date revisions obtained from MolyCorp personnel.

| Mixed RE compounds:       | Dollars per pound |
|---------------------------|-------------------|
| Cerium hydrate            | 1.25-1.40         |
| Cerium oxide              | 1.90              |
| Didymium and RE chlorides | 0.27-0.40         |
| Didymium carbonate        | 1.30              |

All in lots of 50-99 pounds

| Pure oxides:     |             |
|------------------|-------------|
| Cerium oxide     | 4.50        |
| Neodymium oxide  | 30.00-37.50 |
| Europium oxide   | 500         |
| Gadolinium oxide | 85-95       |
| Yttrium oxide    | 44-55       |
| Lutetium oxide   | 3,000-3,500 |

All in lots of 2-99 pounds, 99.9 percent pure

| Metals:                 |       |
|-------------------------|-------|
| Mischmetal, 99.8%       | 3.00  |
| Mischmetal, cerium-free | 5.00  |
| Didymium metals, 97%    | 15.00 |
| Cerium metal, 99.9%     | 20.00 |
| Lanthanum metal, 99.9%  | 27.50 |

All in 50-100 pound lots

| Metal ingots, 99.9%, small lots: |       |
|----------------------------------|-------|
| Cerium                           | 70    |
| Europium                         | 3,600 |
| Lanthanum                        | 70    |
| Neodymium                        | 115   |
| Samarium                         | 160   |
| Yttrium                          | 160   |

Distilled metals: about 50 percent higher than ingots.

Metal powders: in 1-pound lots about \$40-50 per pound greater than the ingot prices for lower priced metals, and \$200-300 per pound greater than the ingot prices for higher priced metals.

Current quotations (Metals Week, Feb. 3, 1969) on bastnasite concentrates, f.o.b. Nipton, Calif., for carloads, per pound of REO contained, are \$0.30 for 55-60 percent REO, and \$0.35 for 68-72 percent REO concentrate. Rare earth oxide, 88-92 percent pure, f.o.b. Nipton, Calif., is quoted at \$0.45 per pound.

## SUMMARY

The rare earth industry, from its humble beginning at the start of the twentieth century as a stepchild of the thorium gas mantle industry, has weathered some romantic and glamorous periods marked by over-optimistic predictions, and now appears to have matured into a dignified and respectable stage, with products of ever-increasing commercial significance.

Some historical landmarks in this development include the production of mischmetal in the early 1900's, the invention of cored arc carbons in 1910, the major commercial development of ion exchange in the late 1940's making possible the production of pure metals on a large scale, the AEC work in the early 1950's on thorium for nuclear reactors which appeared to presage large additional amounts of by-product RE's and led to the search for other raw materials, resulting in the commercial development of bastnasite, the AEC work in the mid-1950's on aircraft nuclear propulsion that required large amounts of high purity yttrium, and finally the commercial fruition of liquid ion exchange in the mid-1960's as an alternative method (to ion exchange) for preparation of high-purity rare earths.

The only RE materials available for many years were mixtures (except for cerium), leading to the traditional product distribution ratio of about one-fourth to cored carbons for arc lighting, one-fourth to mischmetal and cerium metal for lighter flints and some magnesium and ferrous alloys, one-fourth to the glass industry, chiefly in polishing but some in the batch for coloring and decolorizing, and one-fourth divided among many miscellaneous applications. This pattern persisted with little modification until the early 1960's, when it was changed radically by two major new uses: the RE phosphors comprising highly purified europium and yttrium oxides used in color TV tubes, and RE catalysts for catalytic cracking of hydrocarbons, using mixtures of the RE chlorides.

Today the separated, purified RE's account for somewhere between 65 and 75 percent of the dollar value of all RE products sold, although on a volume basis they represent only something under 10 percent of the total. The major use of the mixed RE materials in terms of pounds has become that in petroleum cracking catalysts, with the glass industry also continuing to be a major outlet for the RE's both for polishing and as glass ingredients.

The most important uses at present include phosphors for use in color TV tubes, mercury vapor lamps, and fluorescent lights; superactive catalysts for petroleum cracking, now representing the largest single volume outlet for the mixed RE's; in glass and ceramics, which is an old application but undergoing considerable recent growth; many applications in metallurgy, where the RE's have never reached large volume but in which the potential continues large; in carbons for arc lights, another very old use which has continued to show moderate growth; and completely new outlets, for example, in lasers and permanent magnets which require only pounds rather than tons at present but appear to offer great promise for future development and growth.

The increased availability of the RE's, concomitant with a steady decrease in the price of the purified materials, has stimulated a large amount of application research, and this in turn should continue to promote the growth of the industry. The possibility always exists that one of the many new uses now lumped together under the heading "Miscellaneous" may be a large volume outlet tomorrow.

### ACKNOWLEDGMENT

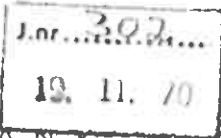
Appreciation is expressed to Messrs. J. L. Drobnick and Paul Kruesi of MolyCorp for their kindness in reviewing the manuscript of this Bulletin.

### BIBLIOGRAPHY

- Altschuler, Z. S. and others, 1967, Rare earths in phosphorites—geochemistry and potential recovery: U. S. Geol. Survey Prof. Paper 575-B, p. B1-B9.
- Anderson, W. Kermit, 1961, Nuclear applications of yttrium and the lanthanons, in *The Rare Earths*, F. H. Spedding and A. H. Daane, Eds., John Wiley & Sons, Inc., New York, p. 522-569.
- Barnard, P. G., 1967, Effects of rare earth additions on plain carbon steel: U. S. Bur. Mines Rept. Inv. 6907, 25 p.
- Baroch, Charles T., 1967, Thorium, in U. S. Bur. Mines Minerals Yearbook, p. 1113-1117.
- , 1968, Thorium: Eng. Min. Jour., v. 169, no. 3, p. 117-119, Mar.
- Bauer, D. J., 1966, Extraction and separation of selected lanthanides with a tertiary amine: U. S. Bur. Mines Rept. Inv. 6809, 13 p.
- Bauer, D. J. and Lindstrom, R. E., 1964, Naphthenic acid solvent extraction of rare-earth sulfates: U. S. Bur. Mines Rept. Inv. 6396, 19 p.
- , 1968, Recovery of cerium and lanthanum by ozonation of lanthanide solutions: U. S. Bur. Mines Rept. Inv. 7123, 9 p.
- Block, F. E. and Campbell, T. T., 1961, Rare-earth and yttrium halides for metal production—chlorides, bromides, iodides, in *The Rare Earths*, F. H. Spedding and A. H. Daane, Eds., John Wiley & Sons, Inc., New York, p. 89-101.
- Bray, Lane A. and Roberts, Francis P., 1967, Separation of cerium from other rare earths: U. S. Patent 3,351,424, issued Nov. 7, assigned to USAEC.
- Bril, K. J., 1964, Mass extraction and separation, in *Progress in the Science and Technology of the Rare Earths*, v. 1, LeRoy Eyring, ed., Macmillan, New York, p. 30-61.
- Brugger, W., and Greinacher, E., 1967, A process for direct chlorination of rare earth ores at high temperatures on a production scale: Jour. Metals, v. 19, no. 12, p. 32-35, Dec.
- Callow, R. J., 1966, *The rare earth industry*: Pergamon Press, New York.
- Cannon, Joseph G., 1969, Bastnasite: Mining Eng., v. 21, no. 1, p. 53-54.
- Carlson, O. N., and Schmidt, F. A., 1961, Preparation of the rare earth fluorides, in *The Rare Earths*, F. H. Spedding and A. H. Daane, Eds., John Wiley & Sons, Inc., New York, p. 77-88.
- Chemical Engineering, 1964, Europium oxide in the red boosts black and white: Chem. Eng., v. 71, no. 25, p. 96-98, Dec. 7.
- , 1967, Expanded markets spur rare-earth technology: Chem. Eng., v. 74, no. 1, p. 32-36, Jan. 2.
- , 1967, MolyCorp: Europium need speedily satisfied: Chem. Eng., v. 74, p. 122-123, Nov. 20.
- Chemical and Engineering News, 1964, Separated rare earth finds commercial use: Chem. Eng. News, v. 42, no. 45, p. 67, Nov. 9.
- , 1965, Rare earths—the lean and hungry industry: Chem. Eng. News, v. 43, no. 19, p. 78-92, May 10.
- , 1967, Process recovers yttrium from residue ore: Chem. Eng. News, v. 45, no. 1, p. 42-43, Jan. 2.
- , 1967, Rare-earth industry still expanding: Chem. Eng. News, v. 45, no. 25, p. 46-48, June 12.
- , 1968, Metals recovery modification promising: Chem. Eng. News, v. 46, no. 12, p. 44-46, Mar. 11.
- , 1969, Face lifting ahead for rare earths: Chem. Eng. News, v. 47, no. 1, p. 36, Jan. 6.
- Chemical Engineering Progress, 1964, The laser—a new tool: Chem. Eng. Prog., v. 60, no. 5, p. 111-112, May.
- Chemical Week, 1966, New light on laser materials: Chem. Week, v. 98, no. 17, p. 74-76, April 23.
- , 1966, Rare earth future glows: Chem. Week, v. 99, no. 15, p. 79-85, Oct. 8.
- , 1967, More rare earths by the ton: Chem. Week, v. 101, p. 51-52, Dec. 2.
- Daane, A. H., 1961, Metallothermic preparation of rare-earth metals, in *The Rare Earths*, F. H. Spedding and A. H. Daane, eds., John Wiley and Sons, Inc., New York, p. 102-112.
- , 1966, Recent improvements in methods of preparing rare earth metals, in *Progress in the Science and Technology of the Rare Earths*, v. 2, LeRoy Eyring, ed., Pergamon Press, New York, p. 23-34.
- Eisenbraun, K. J., and Siever, R. E., 1965, Volatile rare earth chelates: Am. Chem. Soc. Jour., v. 87, no. 22, p. 5254-5256.
- Engineering and Mining Journal, 1968, New discovery may give a shot in the arm to "rare earth" mining: Eng. Mining Jour., v. 169, no. 10, p. 110.
- Eyring, LeRoy, ed., 1964, *Progress in the science and technology of the rare earths*: v. 1, The Macmillan Co., New York.
- , 1966, *Progress in the science and technology of the rare earths*: v. 2, Pergamon Press, New York.
- , 1968, *Progress in the science and technology of the rare earths*, v. 3: Pergamon Press, Oxford, England.
- Gschneider, Karl A., Jr., 1964, Rare earths—the fraternal fifteen: USAEC/Div. of Tech. Information, One of a Series on Understanding the Atom, Oak Ridge, Tennessee.

- , 1968, Technology and uses of beryllium, cesium, germanium, hafnium, niobium, rare earths (including yttrium and scandium), tantalum, titanium, and zirconium: USAEC IS-1757, 158 p.
- Habermann, C. E., and others, 1965, Improved methods for the preparation of the rare-earth metals: *Metall. Soc. Trans., Am. Inst. Mining Metall. Petroleum Engineers*, v. 233, p. 1038-1044, June.
- Harrah, H. W., 1967, Rare earth concentration at Molybdenum Corporation of America solvent extraction plant: *Deco Trefoil*, v. 31, no. 5, Bull. no. M4-B167, p. 9-16, Nov.-Dec.
- Henrie, T. A., and Morrice, E., 1966, A high-temperature electrowinning cell for rare earths: *Jour. Metals*, v. 18, no. 11, p. 1207-1208, Nov.
- Herring, A. P., and others, 1968, The use of rare-earth oxides to give color or visible fluorescence to soda-lime glasses: Presented Am. Ceramic Soc., Chicago, Ill., Apr. 24.
- Hirschhorn, I. S., 1968, Commercial production of rare earth metals by fused salt electrolysis: *Jour. Metals*, v. 20, no. 3, p. 1922, Mar.
- Hopkins, B. Smith, 1939, Chapters in the chemistry of the less familiar elements: Stipes Publishing Co., Champaign, Illinois, Chapter 6: The rare earths including scandium and yttrium.
- Industrial and Engineering Chemistry, 1961, A red phosphor is expected to spur the use of purified rare earths: *Ind. Eng. Chem.*, v. 56, no. 12, p. 9-10, 12, Dec.
- Industrial Research, 1967, Lasers and masers: *Ind. Research*, v. 9, no. 13, p. 67, Dec.
- Johnson, N. L., 1966, Rare earth concentration at Molybdenum Corporation of America: *Deco Trefoil*, v. 30, no. 4, Bull. no. M4-B128, p. 9-16, Aug.-Sept.-Oct.
- Journal of Metals, 1965, Europium for color TV from the newest and largest rare-earth separation plant: *Jour. Metals*, v. 17, no. 8, p. 824, Aug.
- Kanter, J. J., and others, 1962, Yttrium nodular cast iron: *Mech. Eng.*, v. 84, no. 8, p. 35-37; v. 85, no. 3, p. 83-84.
- Kelly, Francis J., 1962, Technological and economic problems of rare-earth-metal and thorium resources in Colorado, New Mexico, and Wyoming: U. S. Bur. Mines Inf. Circ. 8124, 38 p.
- Kleber, Eugene V., and Love, Bernard, 1963, The technology of scandium, yttrium, and the rare earth metals: The Macmillan Co., New York.
- Kremers, Howard E., 1961, Rare earth metals, in *Rare Metals Handbook*, Second Ed., Clifford A. Hampel, ed., Reinhold Publishing Corp., New York, p. 393-417.
- , 1967, Rare earth uses, in *Proc. 6th Rare Earth Research Conf.*, Gatlinburg, Tenn., May 35, p. 1-5.
- Kruesi, Paul R., 1967, Rare earths: *Eng. Mining Jour.*, v. 168, no. 2, p. 151-152, Feb.
- , 1968, Rare earths: *Eng. Mining Jour.*, v. 169, no. 2, p. 136-137, Mar.
- Kruesi, Paul R., and Duker, George, 1965, Production of rare earth chloride from bastnasite: *Jour. Metals*, v. 17, no. 8, p. 847-849, Aug.
- Law, Charles, 1966, Thorium from uranium wastes: *Chem. Eng.*, v. 73, no. 19, p. 172-174, Sept. 12.
- Lengyel, Bela A., 1962, *Lasers—generation of light by stimulated emission*: New York, John Wiley and Sons, Inc.
- Leyer, F. M., and Payne, J. B., 1968, Separation of the rare earths and production of the metals: *Adv. Extractive Metall., Proc. Symp.*, London, 1967 (Pub., 1968), p. 789-804.
- Levine, Albert K., 1963, Lasers: *Am. Scientist*, v. 51, no. 1, p. 14-31.
- Lindstrom, R. E., and Winget, J. O., 1966, Process for separating rare-earth elements by ion exchange: U.S. Patent 3,228,750, Jan. 11.
- Mandle, H. H., and Mandle, R. M., 1966, Uses and applications: in *Progress in the Science and Technology of the Rare Earths*, v. 2, LeRoy Eyring, ed., Pergamon Press, London, p. 190-297.
- Mandle, R. M., and Mandle, H. H., 1964, Uses and applications: in *Progress in the Science and Technology of the Rare Earths*, v. 1, LeRoy Eyring, ed., The Macmillan Co., New York, p. 416-500.
- Moriarty, John L., Jr., 1968, The industrial preparation of the rare earth metals by metallothermic reduction: *Jour. Metals*, v. 20, no. 11, p. 41-45, Nov.
- Morrice, E., and Henrie, T. A., 1967, Electrowinning high-purity neodymium, praseodymium, and didymium metals from their oxides: U.S. Bur. Mines Rept. Inv. 6957, 11 p.
- Morrice, E., and Knickerbocker, R. G., 1961, Rare-earth electrolytic metals: in *The Rare Earths*, F. H. Spedding and A. H. Daane, eds., New York, John Wiley and Sons, Inc., p. 126-144.
- Morrice, et al, 1961, Electrowinning cerium-group and yttrium-group metals: U.S. Bur. Mines Rept. Inv. 5868, 39 p.
- , 1962, Electrowinning molten lanthanum from lanthanum oxide: U.S. Bur. Mines Rept. Inv. 6075, 9 p.
- , 1968, Direct electrolysis of rare-earth oxides to metals and alloys in fluoride melts: U.S. Bur. Mines Rept. Inv. 7146, 12 p.
- Nesbitt, E. A., et al, 1968, New permanent magnet materials: *Appl. Physics Lett.*, v. 12, no. 11, p. 361-362.
- Oil, Paint, and Drug Reporter, 1966, Neodymium—brighter TV: *OPDR*, v. 190, no. 3, p. 35, Dec. 19.
- Overstreet, Wm., C., 1967, The geological occurrence of monazite: U.S. Geol. Survey Prof. Paper 530, 327 p.
- Parker, John G., 1967, Rare-earth elements and thorium in 1967: *Mineral Industry Surveys, Annual, Prelim.*, 2 p., Dec. 21.
- , 1967, Rare-earth minerals and metals: U.S. Bureau of Mines Minerals Yearbook, v. I-II, p. 993-1001.
- Peppard, D. F., 1961, Separation of rare earths by liquid-liquid extraction: in *The Rare Earths*, F. H. Spedding and A. H. Daane, eds., New York, John Wiley and Sons, Inc., p. 38-54.
- Powell, Jack E., 1961, Separation of rare earths by ion exchange: in *The Rare Earths*, F. H. Spedding and A. H. Daane, eds., New York, John Wiley and Sons, Inc., p. 55-73.

- 1964, The separation of rare earths by ion exchange in *Progress in the Science and Technology of the Rare Earths*: v. 1, LeRoy Eyring, ed., New York, The Macmillan Co., p. 62-84.
- Proceedings of the 6th Rare Earth Research Conference, Gatlinburg, Tennessee, May 3-5, 1967. Includes 72 papers and 13 abstracts of papers presented at the conference.
- Rice, A. C., 1966, Fraction separation of aqueous rare earths using amines: U. S. Patent 3,259,472, July 5.
- Schawlow, Arthur L., 1961, Optical masers: *Sci. American*, v. 204, no. 6, p. 52-61, June.
- 1963, Advances in optical masers: *Sci. American*, v. 209, no. 1, p. 34-45, July.
- Shaw, Van E., 1959, Extraction of rare-earth elements from bastnaesite concentrate: U.S. Bur. Mines Rept. Inv. 5474, 12 p.
- Shaw, Van E., and Lindstrom, R. E., 1967, Extraction of euxenite metal values by fusion with ammonium sulfate or ammonium bisulfate: U.S. Bur. Mines Rept. Inv. 6906, 11 p.
- Hebd, E. S., et al., 1964, Continuous electrowinning of cerium metal from cerium oxides: U.S. Bur. Mines Rept. Inv. 6362, 12 p.
- 1966, Electrowinning and tapping of lanthanum metal: U.S. Bur. Mines Rept. Inv. 6882, 10 p.
- Spedding, F. H., and Daane, A. H., eds., 1961, *The Rare Earths*: New York, John Wiley and Sons, Inc.
- Strnat, Karl, J., 1967, Cobalt-rare earth alloys as promising new permanent magnet materials: *Cobalt*, no. 36, Sept., p. 133-143.
- Tapp, N. E., 1965, *The chemistry of the rare-earth elements*: New York, Elsevier Publishing Co.
- Vickery, R. C., 1953, *Chemistry of the lanthanons*: New York, Academic Press, Inc.
- 1967, Laser materials: U.S. Patent 3,340,108, Sept. 5, Appl. July 9, 1963, 3 p.
- Weaver, Boyd, 1968, Liquid-liquid extraction of the rare earths: in *Progress in the Science and Technology of the Rare Earths*, v. 3, LeRoy Eyring, ed., New York, Pergamon Press, p. 129-148.
- Williamson, D. R., and Burgin, Lorraine, 1959, *The rare earths (lanthanons)*: Colorado School Mines Research Found. Mineral Industries Bull., v. 2, no. 1, Jan.
- Winget, J. O., and Lindstrom, R. E., 1958, Amino acids as retaining agents for separation of rare-earth elements on ion exchange resin: U.S. Bur. Mines Rept. Inv. 7175, 8 p.
- Wood, Lyle R., 1968, Electrolytic reduction of rare-earth oxides to mischmetal from a fused fluoride electrolyte: U.S. Patent 3,383,294, May 14, 1968.
- Woysk, Mark M., et al. to American Potash and Chemical Corp., 1967, Recovery of rare earth elements from fluorine-containing material: U.S. Patent 3,353,928, Nov. 21, 1967.
- 1968, Treating phosphate ores: U.S. Patent 3,369,875, Feb. 20, 1968.



November 16, 1970

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It was a pleasure to meet with you and Mr. Eidson on November 6. Mr. Farwell and I enjoyed our discussions and hope that you found them helpful.

It appears that you are faced with a very difficult problem in concentrating the rare-earth minerals from the carbonatite ore which you are investigating. As Mr. Farwell explained, his preliminary microscopical examination of the table concentrate which you sent us indicated that the rare-earth minerals were very finely disseminated, predominantly in the ankerite. Even after pulverizing to minus 270 mesh, very little of the parisite and synchisite were free. The orthite, apparently, was not so finely disseminated, a good proportion of it being free at 270 mesh, with the remainder associated mainly with the barite.

If you feel that we can be of any assistance, we would like to suggest that you send us a 100-pound sample of the raw ore, on which we could conduct some flotation test work here in Stamford. We would propose to test our presently available collectors to determine whether we can achieve any useful separation of the rare-earth containing minerals, and hopefully provide some leads which Mr. Eidsmo could follow up in his own flotation work. If microscopical examination of our test products indicated that we had made any progress, we would probably wish to return samples of these products to you for chemical analysis.

If this suggestion meets with your approval, please ship the sample, preferably crushed to minus 1/2 inch and clearly identified on both the inside and outside of the container, to the attention of Mr. H. Martjens at the following address:

Cyanamid International  
Berdan Avenue  
Wayne, New Jersey 07470  
U.S.A.

Mr. O. Braaten

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November 16, 1970

As I explained to you during our meeting, we do not charge for work of this nature, but the amount of work we can undertake will have to be determined by our initial test results, and by the number of other projects to which our Technical Service Laboratory is already committed.

Yours sincerely,



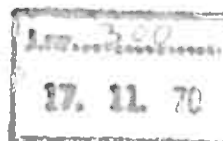
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COLORADO SCHOOL OF MINES RESEARCH INSTITUTE

P.O. Box 112

GOLDEN, COLORADO 80401



November 13, 1970



REF: 10

Mr. Orvar Braaten  
Project Manager  
MEGON  
(Metal Extractor Group of Norway)  
Elkemhuset  
P. O. Box 5430  
Oslo 3, Norway

Dear Mr. Braaten:

This letter is in reference to our discussions of November 9 and contains our proposal for studies on rare earth ore from the Fen areas of Norway.

It is our understanding that your specific current interest is in the development of a beneficiation technique for concentration of the rare earth minerals from the ankerite-calcite-carbonatite type ore. Previous work on this ore and on other ores in the district by your group and others has also shown a high degree of complexity with indicated small grain size and wide dissemination of the rare earth minerals. Preliminary beneficiation tests have confirmed this complexity.

It is apparent that a program to develop process methods for these ores should be quite broad in its initial scope, preliminary objectives being to determine the basic characteristics of the ore. As a first step we would plan a comprehensive ore examination utilizing analytical, microscopic, x-ray, and electron microprobe methods to establish the type and physical characteristics of the valuable and gangue minerals present. Specific objectives of this work would be to obtain information for guiding and planning possible process methods. Mineral liberation sizes, physical characteristics, associations, dissemination, etc., would be of particular interest.

Mr. Orvar Braaten  
MEGON  
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As a parallel effort in this first phase we would also plan a program of exploratory tests utilizing gravity, magnetic, flotation, and other miscellaneous ore dressing methods to gain additional information about the ore characteristics. As a part of this work we would plan to investigate means for the separation of various constituent ore minerals since this approach could provide valuable information on rare earth associations, possibly leading to an effective means of concentration.

Although the above initial program would probably duplicate similar work already done in Norway, we believe that it would be particularly useful to carry out our preliminary studies independently. Later comparison of results then should be quite valuable in the planning of subsequent work.

It is difficult and perhaps inappropriate to propose additional phases of work in this program until the initial phase is completed and we become familiar with the ore. It is quite probable that additional discussions between our respective organizations would be extremely useful at this point to take advantage of the considerable amount of information you have already obtained. We would concur that perhaps one of the best ways to accomplish this would be by means of a visit by our project manager to Norway to discuss the problems in person with your staff members and others who have worked with these ores. However, we believe that any decision on such a visit should await completion of first phase studies.

We would hope that the preliminary program would indicate promising areas for further process research, in which case a second phase of work would be proposed outlining a detailed investigation of the methods. This work usually includes evaluation of process variables, considering both the technical and economic aspects of the treatment conditions. An important part of this work would be the study of additional ore samples to insure the broad capabilities of any proposed process or to determine the need for modifications.

In the final phase of a comprehensive test program it is our usual practice to evaluate the recommended process for the determination of necessary engineering and design data. In some cases, if the process is new or complex, it may be desirable to conduct continuous pilot plant studies at this

Mr. Orvar Branten  
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point. Frequently, however, this is not necessary and sufficient data can be obtained from batch tests to establish economic feasibility and to provide information for engineering design.

The Research Institute is well qualified to undertake this program to any extent that is required. All types of both batch and pilot plant facilities are available and our organization has a long history of successful process development work in virtually all phases of the minerals industry. Staff members have many years of laboratory experience in process research, in most cases preceded by valuable industrial experience. We would be particularly interested in performing this very challenging research program for your organization.

The cost for the initial phase of this program is estimated at between \$7,000 and \$8,000, covering a broad program of petrographic and laboratory tests over an active period of approximately one month. Work could probably be started during the latter part of December contingent upon the time the sample was received and the work authorized. As discussed previously, we will submit our proposal for a continuation of the work after completion of the first phase and more information is available.

Approximately 500 pounds of ore would be recommended as an initial sample. This sample should, of course, be as representative as possible of the main ore body or of the areas of immediate interest. Other small samples representing different types or areas of ore might also be useful to indicate possible variations in characteristics if these are available.

We are enclosing two copies of our research agreement which has been prepared to authorize an expenditure not to exceed \$8,000. Charges will be based on costs incurred in your behalf as outlined in Article II. We would be pleased to discuss any modifications in the contract you feel should be made. If you find it and this proposal acceptable, the project can be initiated by executing a copy and returning it to us.

Mr. Orvar Braaten

MEGON

November 13, 1970

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Your visit and our discussions last week were most interesting and we would be pleased to work with you on this problem to any extent that may be helpful. We will be looking forward to your further correspondence.

Very truly yours,



Robert C. Merritt  
Manager  
Metallurgical Division

RCM:ebm  
enclosure

## AGREEMENT

THIS AGREEMENT, made and entered into this \_\_\_\_\_ day of \_\_\_\_\_, 19\_\_\_\_, between the COLORADO SCHOOL OF MINES RESEARCH INSTITUTE, a corporation not for profit, of the State of Colorado, having an office and place of business in Golden, Colorado (herein referred to as the "Institute") and \_\_\_\_\_ MEGON (Metal \_\_\_\_\_ Extractor Group of Norway) \_\_\_\_\_, duly organized and existing under the laws of the State of \_\_\_\_\_, having an office and place of business in \_\_\_\_\_, (herein referred to as the "Sponsor").

WITNESSETH: That, for the purpose of promoting the increase of useful knowledge and in consideration of the mutual promises and covenants herein contained, the Parties hereto agree, as follows:

1.

The Sponsor hereby engages the Institute to conduct research and development work for the Sponsor relating to preliminary studies of means for beneficiating rare earths ore from the Fen Areas, Norway, as per proposal letter to Mr. Orvar Braaten from R. C. Merritt, dated November 13, 1970, (herein referred to as the "project") for two (2) months period commencing on the day that the Institute assigns one or more of its staff members to the project. The Sponsor agrees to pay to the Institute for its services on this project a total sum not to exceed \_\_\_\_\_  
Eight Thousand (\$8,000.00) DOLLARS

(herein referred to as the "research fund"), and the Institute shall not expend more than said sum without first securing the approval of the Sponsor to do so. The Institute shall use its best efforts in performing the research and development work required under this Agreement.

## II.

The Institute shall charge the Sponsor for the Institute's services on the following basis: (a) the cost of direct labor (including applicable sick leave, annual leave, holiday pay, retirement benefits and one-half of social security cost) of its employees assigned to the project, including all labor performed by the Institute in its service shops and analytical laboratories especially for this project (part time services being prorated); plus (b) 100 percent of this sum of money in lieu of actual overhead, including fringe benefits, unemployment insurance, and group insurance; plus (c) the cost of travel and all other miscellaneous expenses necessary for this project. All supplies furnished by the Institute used in this investigation shall be charged to the Sponsor at the Institute's cost plus a 25 percent handling charge.

## III.

Invoices shall be rendered to the Sponsor by the Institute, as follows: (a) invoices shall be rendered on or about the first of each month and shall cover actual charges incurred on the project during the preceding month including the charge for overhead as defined in Article II; (b) the final invoice shall be submitted for the final month or fraction

thereof promptly after completion of the project. The Sponsor agrees to pay the invoices of the Institute, so rendered, within 10 days after receipt.

#### IV.

In consideration of the availability of the wide variety of equipment now in the possession of the Institute, it is mutually agreed that, in the event that additional equipment shall be required for this project, such additional equipment shall, with the knowledge and approval of the Sponsor, be built or purchased by the Institute, and the cost thereof paid by the Sponsor. It is further agreed that additional equipment so built or purchased shall become the property of the Institute at the completion of the project or upon termination of this Agreement, unless the Sponsor shall, at the time work ceases on the project, request delivery to it of said additional equipment, in which event the cost of packing, shipping, etc. shall be borne by the Sponsor.

#### V.

The Institute agrees to render to the Sponsor, at predetermined periods, written reports of its findings and progress made during the term of the project.

#### VI.

Any and all patentable inventions, applications for patent and patents thereon relating to the subject matter of the project as herein defined, which may be hereafter made by staff members assigned by the

Institute to this project, during the time they are performing work on this project and as a result thereof, shall become the property of the Sponsor, subject to the terms and conditions of this Agreement. The Institute will make such agreements with personnel it employs on the project as to insure conveyance of all rights to Sponsor, including signatures of such personnel as may be required to effect the intent of the preceding sentence. The Institute shall cause to be kept complete and systematic memoranda in writing, including notes on all experimental and research work, descriptions, diagrams, and other data, pertaining to inventions relating to said subject matter made while working on said project and resulting from work thereon, which memoranda shall be available at all times to the Sponsor. In the event that the Sponsor desires to keep secret any new process, article, machines, or composition of matter, relating to the project, invented by staff members assigned to the project and as a result of their work thereon, the Institute shall use its best efforts to maintain said inventions secret and not to disclose them to anyone without the consent of the Sponsor.

#### VII.

It is also agreed that no advertising, promotional, or publicity matter containing any reference to the Institute or to the Colorado School of Mines, or to any of their employees, shall be made use of by the Sponsor or anyone in the Sponsor's behalf, unless and until the same shall have first been submitted to and received the approval of the Direc-

tor of the Institute.

VIII.

In the event that the research fund provided for in Article I hereof is expended prior to the expiration of this Agreement, the Institute shall discontinue work on the project and this Agreement shall terminate, unless the Sponsor, prior to the date on which work is to cease, authorizes the Institute, in writing, to continue work on the project and agrees to pay the cost of such additional work in accordance with the terms of this Agreement. Should the work on this project be completed to the satisfaction of the Sponsor before the research fund is expended, the Sponsor shall have the right to terminate this Agreement.

IN WITNESS WHEREOF, the Parties hereto have caused this Agreement to be duly executed by their duly authorized officers the day and year first above written.

COLORADO SCHOOL OF MINES RESEARCH INSTITUTE

By *Wander*  
Director

MEGON  
(Metal Extractor Group of Norway)

By \_\_\_\_\_

Title \_\_\_\_\_

100-304.....  
20. 11. 70

# THE GALIGHIER COMPANY

ESTABLISHED 1901



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359-8731

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SALT LAKE CITY, UTAH 84110

U.S.A.

ARRA CODE 201

November 13, 1970

Mr. Orvar Braaten  
A/S Megon  
Elkemhuset  
P. O. Box 5430  
Oslo 3, Norway

## Upgrading of Rare Earth Minerals from Norwegian Ore

Dear Mr. Braaten:

We appreciated the opportunity of discussing with you and Mr. Eldsmo the problems encountered in attempting to upgrade the rare earth minerals in the Fen ore. From the report by Mr. Marcus Digre, Associate Professor of Mineral Dressing, and our discussions, evidently no effective beneficiation procedure has been developed. In a major portion of the ore body, the rare earth minerals are intimately associated with the hematite in a size range that would be virtually impossible to liberate. However, in one section of the ore body the rare earth mineralization is much coarser. This is the portion of the ore body from which the sample has been taken for the proposed beneficiation studies.

Our scope of beneficiation studies would include only flotation. We would examine various reagent combinations and procedures which, as indicated by our past experience, could possibly activate and collect the rare earth minerals. The initial testing would involve the use of fatty acid collectors with dispersing agents that have been effective on ores with similar mineral character. Possibly the testing would involve the selective removal of gangue components prior to the rare earth recovery or possibly the rare earth minerals could be recovered along with a carrier mineral such as hematite.

If possible, the concentrates produced in the laboratory will be examined under the microscope and compared with samples of relatively pure minerals obtained from you. Samples of products from all will be retained in our laboratory. Samples from selected tests will be sent to you, via airmail, for analyses and communications maintained by telex.

LEADERS IN EXPERIENCE AND SERVICE

AIR  
MAIL

THE GALIGHER COMPANY

Mr. Orvar Branton  
A/S Magon

- 2 -

November 13, 1970

The time interval required for mailing samples, assaying and receiving results, will to a large extent govern the rate at which the program proceeds. As testing proceeds there will be times when it would not be prudent to proceed without knowing results of previous tests.

We estimate that our charges will be \$800 to \$1,000 per month. The charges are based on \$10 per hour for sample handling and preparation, and \$15 per hour for testing and reporting. Miscellaneous charges such as outside microscopic studies will be at cost plus 10%.

A progress report will be submitted to you each month along with an invoice for the previous months' charges. Meetings as necessary can be arranged and our laboratory will be open to your engineers and suggestions.

Under separate cover we have mailed by airmail, printed matter, the various Galigher bulletins requested.

We are looking forward to working with you on this project.

Very truly yours,

THE GALIGHER COMPANY



H. A. Dawson  
Metallurgist



H. A. Johnson, Manager  
Metallurgical Sales

HAD/HAJ:rlb

BESØK VED U.S. BUREAU OF MINES RESEARCH STATION, RENO,  
NEVADA, 11.11.1970

Deltagere fra Megon:      Odd Eidsmo og Orvar Braaten

Vi møtte følgende:      Dr. T.A. Henrie  
                                 R.E. Linstrøm  
                                 M.M. Wong  
                                 Prof. J.S. Winston  
                                 J.W. Walkiewicz  
                                 J.J. Sjöberg  
                                 E. Morrice  
                                 E. Aamland

Mr. M.M. Wong som har overtatt dr. T.A. Henriess stilling som leder for instituttet viste omkring. Vi besøkte anleggene for elektrolytisk fremstilling av legeringer med sjeldne jordarter og ren-metallfremstilling, produksjon av magneter og foretok et ganske kort besøk i deres ekstraksjonsavdeling.

Cand. real. E. Aamland hilste vi også på, han er nå igang med sitt arbeide i henhold til planen, men har bare vært i virksomhet i et par måneder ennå. M.M. Wong fortalte oss at han i privat brev fra professor K. Grjotheim har fått vite at professor Grjotheim selv vil tilbringe 6 måneder (sabbatical -1/2-year) ved instituttet isteden for dr. Lützow-Holm. Dette har professor Grjotheim ikke fortalt oss noe om.

Det var lite av verdi å hente i Reno når det gjelder oppredning av Fensmalmen. Vi etterlot 4 mineralprøver hos J.J. Sjöberg som har utført en spektrografisk analyse av materialet. Denne viste seg, da vi mottok rapporten, imidlertid å være av meget begrenset verdi.

Orvar Braaten

OB/kk

11.12.70

Ad: Dr. Brantenhusk i Sonx i 1970. = 21. november 1970

# I Dagsprogram.

Søndag 22-11-70:

Branten, Smidt og Sidmo startet fra kl. 12.00. Ankom Lille-  
strand kl. 18.45. Sidmo og T. Branten tokom til hot. Vi  
diskuterte enkelte sider ved Foss og gikk til kl. 21.00.

Mandag 23-11-70:

Vi ankom til A.S.Q.-anlegget kl. 8.00. Branten, Smidt, Sidmo,  
Ingebratsen og S. Branten foretok en kort tur i området A, B, C og D.  
Smidt hadde en kort forelesning om Foss og Branten petrografi  
og mineralogi.

Kl. 10.30 til pålysning med S. Branten i Laskelund og besiktiget.  
Vaskeriet og k. rotte-floresjone var i full drift.

Efter en hyggelig lunch, fra av de nye Branten, Smidt og  
Branten, Smidt og S. Branten. Vi gikk til T. Branten, besiktiget  
hans mineralforretning og utpev. Smidt kjøpte en rotte  
mineralprover fra T. Branten.

Kl. 16.00 besøkte vi direktør Branten på hans kontor. Smidt  
kjøpte prøver av indolitt, olivinit og sveditt. Branten  
orienterte oss om de nye Branten og Smidt. Vi gikk til  
mineral-konsentratene fra A/S. Branten. 1/3 av dem var indolitt  
i de nye Branten. Smidt og S. Branten, som hadde vært  
oppmerksom på at de nye Branten var interessert i å kjøpe indolitt-  
innholdet. Branten gikk på Fl. og Smidt var  
interessert i indolitt-mineralene. De nye Branten hadde  
utnyttet i den nye Branten oppslutning. Branten ga uttrykk  
for sin skuffelse over at Branten i sin tid hadde forleitet ham til  
å kjøpe opp mineralene. Branten hadde en sende inn en  
oppgave over lageret og gi et tilbud på mineralene. Dette tilbud  
ville så bli vurdert av A/S. Branten.

Vi ankom til Lillestrand kl. 19.00. Etter middag ble selskapet  
invitert til direktør T. Branten. Ansettelsesproblemer ble knapt  
berørt. Sidmo hadde nyttet dagen til å sette seg inn i A/S. Branten  
prosesser på A.S.Q.-anlegget. Sidmo og T. Branten diskuterte  
disse ting i løpet av aftenen.

Tirsdag 24-11-70:

Vi startet fra Lillesand kl. 7.00. Ankom Fensfeltet kl. 10.30. Besøkte kontorene hos A/S Korsk Bergverk og ble vist et utvalg av Fensfeltets bergarter. Smidt og Østmo fikk enkelte konsentrat-prøver av koppitt av Haugen til nærmere undersøkelser. Vi inspiserte så hematittmalms-årer, rødberget og rauhaugittberg-artene i Vegohjellingen og i Solladalen. Smidt ble orientert om malmenes generelle karakter, mineralogi og geologi. Vi samlet inn endel prøver av hematittmalms, rødberget og rauhaugitt.

Kl. 12.00 vendte vi tilbake til A/S Korsk Bergverk. Her hilste vi på bergmester Øvre. Deretter besøkte vi hyestoretsgodvokst-Kaasen. Helt selvsagt deltok så i en lunch hos godseier Cappellen og frue.

Kl. 14.00 reiste vi igjen ut i feltet. Vi besiktiget opprednings-anlegget for søvitt-malm. Desuten ble samtjærnitter og søvitt undersekt i felt.

Kl. 15.00 reiste vi fra Fensfeltet og ankom Oslo kl. 19.30. Vi ble invitert hjem til O. Branten der fru Branten tok hånd om oss på beste måte. Branten sørget for at Smidt kom til Grand Hotell og Saks til Kilo. Videre reiste til Trondhjem med fly senere på ettermiddag.

Onsdag 25-11-70:

Branten, Smidt og Saks startet fra Trondheim kl. 7.30. Ankom Varna kl. 8.15. Ankom Trondheim kl. 9.15.

Vi hilste på Ingvaldsen, Kvalheim, Svinndal, Ryningjord, Digre og Krogh. Konferansen ble innledet av Branten med en kort orientering om bakgrunnen for Smidts besøk i Norge.

Smidt orienterte klart og grundig om Hazen Research Co. Han redagjorde for hvordan Hazen Research tidligere hadde løst en rekke "benefication problems" av tilkøende art som den man møter i Fensfeltet. Svinndal redagjorde for hvordan beringsen var utført; om prinsippene for prøvetakingen og generelle trekk ved bergartenes petrografi og mineralogi.

Kvalheim redagjorde inngående for prepareringen av prøvene til uttak av det endelige analyse-materialet.

Smidt eksaminerte inngående Svinndal og Kvalheim på dette punkt. Det er nå klart at gjennpør av alle uvalgte prøver (fra 2-5 m) foreligger på NGU. Prøvene er knust ned til 4-10 mm.

Smidt redagjorde kunngjøring for utgivelse av "Composite sample" av A. I. nr. 2 (25. 11) av Oslo 1. side. For-  
von blev bledd og opplyst at det i den 2. side. 2 sider la ved.  
1 del sendes av "Ullt til Rosen" av "Oslo" til en store vel  
presiseret og avpassede undersøkelse. 1 del undersøkes ved  
Institutt for Geologi.

Digre redagjorde for Oppredningslaboratoriets orienterende opp-  
redningsforsøk av rødbergsula, hemmelig-ula og rødhaugitt-ula.  
Krogh redagjorde for X-ray mikroskopiske analyser av preparater av  
de nevnte maltyper.

Etter møtet ble alle forsamlingen innkalt av Smidt, Smidt,  
Dræsten, Svinnel og A. I. Smidt ble bledd av rødhaugitt-  
ene og de typiske rødbergs-bergarter av karakteristikk. Selv om  
de lokale variasjoner i sammensetning og mineralogi etc. er til-  
dels meget store, vil disse variasjoner utgjøre ved begynnelse og  
behandling av store mengder materialer. Smidt bledd av "Composite  
sample" av A. I. nr. 2 etter at det ble bledd vil komme meget nær i  
sammensetning og karakter til det gode mal vil bli behandlet ved  
et oppredningslaboratorium. Derfor er det av ytterste viktighet å  
undersøke denne "Composite sample" så grundig som overhodet mulig.

Etter møtet på VOU reiste vi klokken 11. 14.30 avla vi en  
visitt på Oppredningslaboratoriet. Alltid vi møtte var Dræsten,  
Digre, Krogh, Elden, Smidt og A. I.

Digre redagjorde for sitt syn på Oppredningslaboratoriet. Digre bledd meget  
kategorisk at dersom det ikke var mulig å utnytte europiuminnholdet  
var det ingen grunn til å arbeide med Oppredningslaboratoriet. Ved siden  
av europium mente han at europiuminnholdet hadde en viss økonomisk be-  
tydning. Innholdet av europium var en stor interesse i Pans-  
feltet etter Digres mening.

Etter at de kjemiske, mineralogiske og oppredningstekniske sider  
ved Pansfeltet var diskutert, ble Glendendeproblemet tatt opp  
til drøfting. Elden diskuterte raskt hva som måtte gjøres. Dette  
ble bifallt av Digre og Krogh.

Digre understreket at de ting Elden nevnte hadde vært en forut-  
setning for en effektiv utvinning av xenotim.

Etter møtet viste Digre oss rundt på hele instituttet.

Vi reiste fra Erendhjem ca. kl. 16.00 og ankom Oslo ca. kl. 19.10.

Torsdag 26-11-70:

Kl. 10.00 ankom kantonen og Smidt til Institutt for Geologi. Vi nyttet tiden til å gjennomføre en rask konsentrasjon og mineralprøver samt bergartprøver av radius lte.

Kl. 11.50 besøkte vi Geologisk-Mineralogisk Museum og talte med professor Neumann. Vi beså deretter en del norske mineraler i samlingene.

Kl. 12.30 besøkte vi Institutt for Kjemiskjordi og talte med Alstad. Alstad viste oss de viktigste laboratorier og instrumenter. Vi fikk se hvordan cand. real. Samt bestente europium i ortinit-konsentra. fra Vaskjering. (Ornitien viser 0.07, 2u).

Etter besøket hos Alstad, vendte vi tilbake til Institutt for Geologi.

Kl. 15.30 møttes vi på professor Tuxen's kontor. Her ble orientert om det som var passert i løpet av Smidts opphold i Norge. Her ble stilt en del spørsmål vedrørende de undersøkelsesplanene som kunne tenkes set i anvendelse i Fensholt.

Smidt redegjorde også for mine synspunkter. Det ble konkludert med at Smidt skulle på basis av disse forslagene, levere et detaljert forslag til A/S kanton om hva Hagen Research Co. vil kunne utføre av undersøkelser som enten ville kunne løses hurtigere eller bedre av Hagen Research Co. enn vi selv ville kunne gjøre.

Resten ble høvet kl. 16.30.

Oslo, 4. desember 1970

*P. H. Salte*  
P. H. Salte

Dr. Smith foreslår følgende rækkefølge ved de første AF-undersøttelser i Fossfeltet.

Dr. Smith foreslår på hvert nyt felt med første foretak en orientering om hva Hazen Research Co. er og hvordan rede for de prinsipper som han mente burde legges til grunn for undersøkelsen av AF-karbonatittene i Fossfeltet.

- A. Fremstilling av en "composite sample" som best mulig skal representere det rågode som vil bli i prosessen i et oppredningsanlegg.  
Slikt la skyve vekt på at det er uunngåelig nødvendig å fremstille en slik prøve. I det et fall ville det kunne regne med et langt mer tidkrevende undersøkelsesarbeid.
- B. Utføre en fullstendig mineralogisk klassifisering av samtlige mineraler i composite sample.  
Slikt understreket at dette var i første trinn i undersøkelsen. Praktisk sett alle andre undersøkelser utsettes inntil de mineraler ikke bestemmelse er fullført.
- C. Gi en fullstendig kvantifisering av innhold i % av enkelte AF-mineraler og AB-mineraler i "composite sample".
- D. Fremstille rene koncentreter av AF-mineralene og AB-mineralene, samt alle kvantitative sett av AF- og AB-mineraler fra "composite sample". På basis analysert av disse, kunne gi en fullstendig oversikt over AF- og AB-fordelingen i "composite sample".
- E. Foreta en nøyaktig analyse av fordelingsforholdene av alle kvantitativt sett viktige mineraler og deres friinnholdsgrad ved varierende smeltevarmer.
- F. Foreta petrografiske og mineralogiske studier av et representativt antall prøver for en mulig å skaffe informasjoner om de økonomisk viktige mineralers oppførsel i karbonatittene.
- G. På basis av alle disse undersøkelser trekkes den opp linjene for oppredningsforsøkene.

Slikt presiserte at alle slike forsker står under løpende mineralogisk kontroll i Hazen Research Co. I det øyeblikk en prosess er funnet, er det oppredningseksperimentenes neste oppgave å optimalisere

prosessen og konstanter nødvendige for prosessen.

Smidt påpekte disse punkter med praktiske eksempler fra en rekke forekomster av slike typer som RE-karbonsatittene i Fensholtet.

Han presiserte at det i de forskjellige undersøkelsesperioder var mulig å benytte seg av en rekke forskjellige prosesser for å isolere og bestemme mineraler i bergarter og konsentrater. Disse prosesser tilhører Hazen Research Co. og kunne ikke anføres utdypet. Han hevdet meget tydelig at systematiske undersøkelser, meget sjelden førte til brukbare resultater, og at det alltid kan være nødvendig å legge over et program i henhold til de problemer man står støttet på når det gjelder komplekse malmer og mineralforekomster.

Mitt personlige inntrykk er det at Dr. Smidt kvalifikasjoner er meget positive.

Det viste seg også på gang at vi talte nøyaktig det samme språk. Vi har det samme prinsipielle syn på det gjelder undersøkelsesprogrammet for Fensholtet. Jeg har arbeidet og arbeider fortsatt etter de samme linjer som Smidt skisserte.

Dr. Smidt har imidlertid en rekke spørsmål til meg om det i mitt arbeid. Dette vil si at han vil kunne få noen resultater langt hurtigere enn noen annen institusjon i vårt land.

Det som skiller meg fra Dr. Smidt er at han har et mye større utvalgt utvalg av prøver som vil bli sentrert undersøkelsene til å gjøre "composite samples", mens jeg har lagt merke til undersøkelsene om de bredere områder. Smidts forslag til mitt opplegg var at jeg ville bruke de lang tid for å gjennomføre opplegget. Dessuten gir Smidt også mer direkte ut på å få svar på hvorvidt RE-karbonsatittene er "malin" eller "ikke malin". Dessuten også i vil felle "malin" hvordan malmen best skal kunne oppredes.

Det sier seg selv at dette er hovedsakelig punktet også for mine undersøkelser, men Smidts stas og hans egne erfaringer vil nok føre mer direkte til målet enn mine mer bredt anlagte undersøkelser.

Blindern, 1. desember 1970

P. Chr. Sævi  
P. Chr. Sævi

# HAZEN RESEARCH, INC.

1. nr. 3. 1. 1. ....  
09. 12. 70

4801 INDIANA STREET  
GOLDEN, COLORADO 80401  
TELEPHONE 303/279-4501

December 4, 1970

A/S Megon  
Metal Extractor Group of Norway  
Elkemhuset  
P. O. Box 5430  
Majorstua  
Oslo 3, Norway

Re: Proposal to determine the quantitative rare earth mineralogy of  
drill core No. 2 from the Fen deposit.

Dear Mr. Braaten:

This letter will confirm the discussions concerning the Fen project between associates of A/S Megon and Mr. Roland Schmidt of Hazen Research, Inc. during his recent visit in Norway.

During this visit Mr. Schmidt had an opportunity to become acquainted with the technical personnel who have previously been engaged in various phases of the study of Fen carbonatite. In addition, the Fen area itself was visited as well as the Norwegian Geological Survey in Trondheim where three diamond drill cores from Fen were examined.

As a result of this review the decision was made that the next essential step in the Fen project is to determine the quantitative rare earth mineralogy on drill core No. 2. This core consists primarily of carbonatite (rauhaugite) and apparently represents rather typical ore.

We propose that Hazen Research undertake for you this quantitative mineralogical study in accordance with the following outline.

1. Quantitative concentration of rare earth minerals in order to determine:
  - a) actual percentage of rare earth minerals present
  - b) identity of the rare earth minerals
  - c) chemical distribution of rare earth elements in these minerals
  - d) range in particle size

December 4, 1970

The preparation of a representative composite sample of the entire drill core No. 2 should be done at the N. G. U. laboratories in Trondheim. Since this core has already been split in half for assay purposes the minus 10 mm reject obtained in sample preparation could be used for this purpose.

The method used to obtain a concentrate suitable for these determinations will be through selective leaching, at coarse particle size, taking advantage of the relative insolubility of the R. E. fluorocarbonate minerals in weak acids. Small scale physical beneficiation methods will be employed only where absolutely necessary. The selective leaching will be done with the raw ore at relatively coarse particle size so the natural crystal size of R. E. minerals will not be destroyed.

From these fundamental data it will then be possible to choose the type of commercial beneficiation process and to some extent the conditions necessary for upgrading this ore. In addition, it would then be possible to estimate what grade of R. E. mineral concentrate and recovery could be expected.

It is estimated that this work can be started in the beginning of January, 1971, provided the composite sample is available, and will be completed within three months. The expenditure for this work will be approximately \$2,000 per month not to exceed \$6,000 total. Monthly progress letter reports will be issued with a final report after completion of this work.

I hope we will have the opportunity to undertake this work for you and we are enclosing a standard form of Professional Services Agreement for your consideration. If it would be simpler for you from a business point of view to have the work accomplished on the basis of a Purchase Order from your company, this would be entirely satisfactory with us.

Very truly yours,

Wayne C. Hazen  
President

WCH:mp  
Enclosure