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OCCURENCE AND EXTRACTION OF RARE EARTHS IN nORWAY

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## OCCURRENCE AND EXTRACTION OF RARE EARTHS IN NORWAY

B. Gaudernack and O. Braaten, A/S Megon, Norway

### 1. INTRODUCTION

The Norwegian Rare Earth Research Group was established in 1967 upon the initiative of the Royal Norwegian Council for Scientific and Industrial Research. The Council has a policy generating function and is also an advisory board for the Government in matters of distribution of financial support mainly to research in applied science and technology. The initiative came as a "spin-off" from a broad study of Norway's competitive future situation in view of the rapid technological development. Up until recently the country's main indigenous advantages for industries have been abundant cheap electric power, many good icefree deep water harbours, plenty of fish in coastal waters, extensive forests, and some minerals in the mountains. These natural advantages appear today to be loosing in significance. A critical examination of the country's conditions revealed that in order to maintain its high standard of living for its small population it might be necessary to develop industrial capabilities within advanced, sophisticated fields where short distances to markets, extensive national mass production units and other conditions characteristic of large continental countries would be less significant.

Such considerations led the Council's Metallurgical Committee to venture into a practical test project. It was in November 1966 decided to investigate the potentialities for the production of Rare Earths, explicitly because this is within an exclusive field, in a technological, advanced environment, and a typical small volume manufacture of fairly high priced products.

By coincidence the Norwegian Institute for Atomic Energy had at that time just brought to an end its pilot-extraction of plutonium from spent uranium fuel elements. As it was found that the technology of liquid-liquid-extraction was a promising process for rare earths, it was decided to place the task of rare earths production with the same team which had developed the plutonium extraction.

The Council engaged several science institutions in a preliminary survey. Among them were: The Norwegian Geological Survey, the Institute of Geology at the University in Oslo, the Mineralogical-Geological Museum, the Institute of Inorganic Chemistry at the University in Trondheim, the Institute of Nuclear Chemistry at the University in Oslo, the Mineral Dressing Laboratory at the University in Trondheim, the Central Institute of Industrial Research, and as mentioned above the Institute for Atomic Energy.

In addition the Science Council engaged an American consultant firm for an industrial market survey on the uses of rare earths, with special emphasis on yttrium and europium.

On this basis the Science Council invited 10 major Norwegian industrial companies to form the Research Group for Rare Earths, which was established in May 1967. Its main objectives are:

1. to investigate indigenous rare earth deposits and evaluate their potential as raw materials for rare earth production,
2. to develop the technology for, and evaluate the feasibility of such production,
3. to study the market developments for various rare earth products.

The project led in April 1969 to the establishment of the company A/S Megon & Co. (Metal Extractor Group of Norway), which is at present operating a pilot plant for extraction with a capacity of 5 tons yttrium oxide per year and an ore beneficiation plant for the production of the equivalent amount of xenotime concentrate.

Over the 5 years that the project has been run now approximately \$ 2 mill. have been invested, half of which has been from Government funds. The public grants have been given on the condition that they be paid back over a period of time, when and if the industrial application of the research work does show a profit after ordinary depreciation, taxes and interest on loans. If no commercial profitable activity does come out of the research work the claims are waived.

In 1968 and in 1971 respectively feasibility studies were carried out on a commercial scale plant with 30 - 50 tons yttrium oxide per year capacity. These feasibility studies showed a satisfactory return on investment under competitive conditions. The project is therefore proceeding with plans for such production.

## 2. GEOLOGY AND MINERALOGY OF NORWEGIAN RARE EARTH DEPOSITS

Occurrences of rare earth minerals in Norway have been known since before 1840 from the investigations of W. C. Brøgger, A. Bugge, V. M. Goldschmidt, H. Bjørlykke and others. Thus the pegmatites in Evje, Setesdalen and Langesundsfjorden, and several other Norwegian deposits have been described in a great number of mineralogical geological publications. So far, however, they have been regarded by many partly as curiosities, partly as scientifically interesting specialities. No investigation was carried out with industrial activities in mind until the Rare Earth Research Group started this project. The present investigations have covered between 100 and 200 deposits of rare earths in Norway, distributed over practically the entire country. From among this large number three have been selected for particular and extended investigations.

### 2.1. Glamsland - A Rare Earth containing pegmatite deposit

At Glamsland approximately 3 km N of the town Lillesand in the south of Norway the company H. Bjørum in 1968 opened up a feldspar operation producing 70.000 tons of concentrate per year.

In general the strike of the supra crystal rocks are NE/SW within large areas surrounding the Glamsland deposit where the strike of the metase-





Figure No. 1. Aggregate of xenotime crystals in biotite-albite-quartz.

diments are more N - S. This change of the general strike directions was caused by strong tectonic movements in the earth's crust. These tectonic movements forced the metasediments to split along the schistosity planes by differential movements of the various layers. The pegmatite magmas were now able to intrude and form the large conformable pegmatite lenses of the Glamsland area.

The various structures of the pegmatites are remarkably well preserved. Some post genetic fractures and quartz veins are found, but in general no effects of important geological processes are observed microscopically. Nevertheless, microscopical and chemical examinations show rather clearly that some metamorphic processes have occurred.

These processes took place in shallow depths and at moderate temperatures and caused strong unmixing of the two feldspars, Na-feldspar and K-feldspar, into discrete grains of microcline and albite. The texture of the rock became more granular xenomorphic with more clean cut grain boundaries.

The pegmatites have the same chemical composition as that of normal granites. The mineralogy is simple. The chief minerals are oligoclase, microcline, quartz and minor amounts of biotite, muscovite, garnet and rare earth minerals.

The rare earths in Glamsland occur mainly in the minerals xenotime, garnet and monazite. The recovery has been concentrated on yttrium from xenotime,  $\text{YPO}_4$ . The mineral occurs in idiomorphous crystals of up to 3 mm size, and down to less than 0,1 mm. The crystals are closely associated with the biotite rich aggregations and zones in the pegmatites. Figure No. 1 shows such an aggregate of xenotime crystals in biotite-albite-quartz.

The yttrium content in the raw ore is in general analysed to be approximately 150 parts per million of which approximately 70% is contained in the xenotime and monazite. The balance is taken up by the garnet.

The following analysis of a sample of granite from Glamsland shows the distribution of some of the rare earths:

| Y<br>ppm | La<br>ppm | Sm<br>ppm | Eu<br>ppm | Yb<br>ppm |
|----------|-----------|-----------|-----------|-----------|
| 200      | 10        | 4         | 1         | 30        |

Based on experimentation over two years the xenotime concentrate is now being produced from a mica rich waste which is being discarded from the feldspar operations. This xenotime rich mica waste contains approximately 0,1 - 0,3% yttrium.

It was treated experimentally with a number of methods such as flotation, high intensity magnet separation, gravimetric separation on washing tables, electrostatic separation etc. The present test operation is based on a washing table treatment followed by drying. A concentrate containing approximately 5% yttrium has been obtained by this simple method. It is feasible that even higher concentrations may be obtainable in a two step washing table operation. However,

this may lower the yield which now amounts to some 60% of recoverable xenotime. Most of the losses are in the slimes. After drying to max. 1% water content the concentrate is being transported to the extraction plant in special containers.

## 2.2. Ødegaarden - A Rare Earth containing apatite deposit

Situated just south of Feset, approximately 100 km south of Oslo, Ødegaarden's verk was a thriving mining centre for many years. In this district numerous phosphate-bearing veins cut the Precambrian metamorphic rocks. Discovered in 1872, the phosphate deposits were mined by a Norwegian and a French company ("Compagnie Francaise de Mines de Bamle"). Between 1872 and 1918, a total of 150.000 tons of phosphate were produced. Owing to low prices and a failure to find new veins, mining has long since stopped.

The phosphate veins outcrop along the SE slopes of a NE-SW running valley. The hills on both sides of the valley are composed of banded amphibolites (in parts garnetiferous) with rare, thin quartzite bands; these rocks strike NE-SW and dip steeply to the SE. A mass of scapolite-hornblende metagabbro (the classic Ødegaardite), 850 m long and 30 to 70 m broad, outcrops in the valley bottom. This rock shows relict igneous textures and contains abundant scapolite, hornblende, and rutile, with subordinate amounts of augite, tremolite-actinolite, chlorite, epidote, plagioclase and apatite. The metagabbro exhibits no sharp contact with the surrounding amphibolites; the contact being transitional. It is probable that some of the amphibolites adjacent to the mass represent an advanced stage in the metamorphism of the same gabbro.

Concordant and discordant phosphate-bearing veins (up to 4 m thick) crop out along the SE side of the valley, both in the amphibolites and in the metagabbro. Today only a few mines are available for study owing to collapse and flooding. The mines reached a depth of around 150 m. The veins which can be seen now, strike NE-SE, dipping at around 30° south-eastwards.

Under the project the many gangues, shafts and addits have been copied from old mining maps and records from the operations. Fresh apatite samples from 30 meter below the surface have been taken from the rock phase and analysed.

The Ødegaarden apatite is a chloro-apatite. A typical sample shows the following composition with respect to rare earths:

| Y<br>ppm | La<br>ppm | Sm<br>ppm | Eu<br>ppm | Yb<br>ppm |
|----------|-----------|-----------|-----------|-----------|
| 3100     | 700       | 500       | 40        | 200       |

This means that apatite from Ødegaarden contains at least 10 times as much yttrium as f. i. the Kola-apatite and roughly the same content of europium.

However, recovery of the yttrium from the Ødegaarden deposit would only be practical in connection with the exploitation of the remaining apatite in the deposit as a source of phosphorous. There are at present no such plans under consideration.

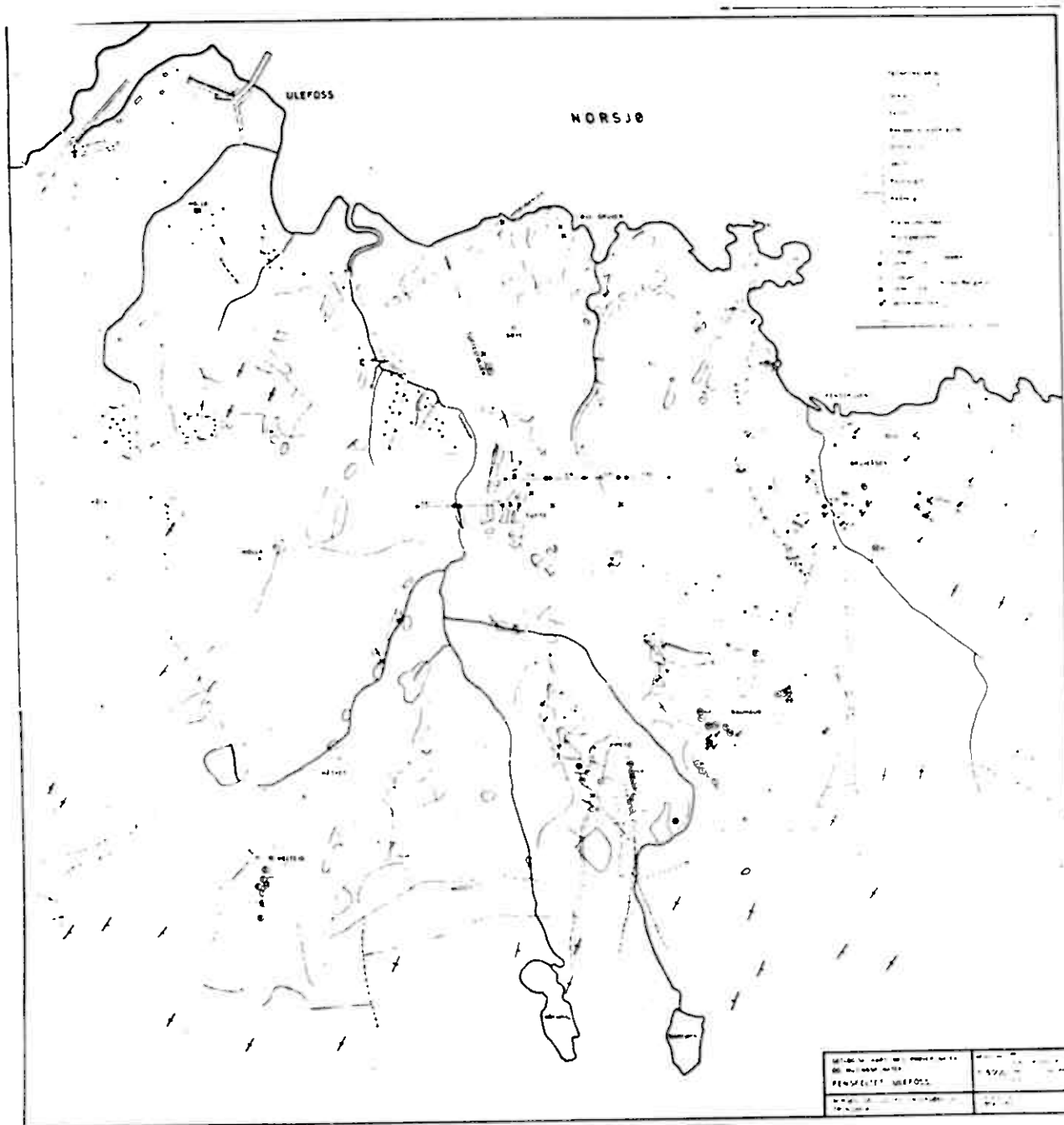


Figure No. 2. The rock complex of the Fen area.



### 2.3. Fen - A hematite-carbonatite deposit containing thorium and Rare Earths

Fen lies near Ulefoss in Telemark, 119 km southwest of Oslo and 12 km west of the geological boundary of the Oslo Region. The pre-cambrian basement in the area has been invaded by peralkaline rocks and carbonatites over an area of about 5 square kilometres. Figure No. 2 shows a simplified map of the rock complex of the Fen area.

Fenite is an alkali syenite with the main minerals in the rock being alkali feldspar, partly as a characteristic micropertthite, aegirine, aegirine-augite and minor Na-amphibole. Apatite, zircon and pyrite occur as accessory minerals.

Urtite-ijolite-melteigite-vipetoite are rocks with a content of nepheline, pyroxene, biotite, aegirine-augite, amphibole, and other minerals. They have partly a hypidiomorphic texture and thus resemble igneous rocks.

Søvite which forms a main part of the Fen area, is a carbonate rock of variable composition. Ankerite and dolomite occur in variable amounts and in places can become quite dominant, in which case the rock is called rauhaugite. Mica minerals, magnetite, pyrochlore and apatite are found in the søvite in variable quantities.

Rødberg ("red-rock") is a carbonate rock which is red-coloured due to finely dispersed hematite formed by iron pneumatolysis and has been the basis for the Fen mines. Some of the dyke-like masses show a high radioactivity and an average content of 0.2% Th and approximately 2% rare earth oxides.

Kimberlite (Damtjernite) occurs in dykes, dyke-like bodies and as kimberlite breccias in volcanic plugs. This rock occurs both in the complex and outside it. The kimberlite is the only rock in the Fen area which can be said with certainty to be of igneous origin.

The Fen mines were in production from 1652 to 1927 and approximately one mill. tons of iron ore have been mined here. The ore is a hematite ore which occurs as N-S trending dykes and lenses in the large "rødberg" area in the eastern part of the complex. Containing over 100 mill. tons of carbonatite with a fairly high content of thorium this represents one of the largest known resources of thorium in solid rock in the world.

The Norwegian Government operated the Søve mine from 1953 to 1964, producing niobium concentrate from the pyrochlore bearing søvites.

Under the project of the Rare Earth Research Group an extensive exploration of the area was undertaken, mapping the distribution of rare earths including some diamond drilling. A typical analysis of hematite from Fen shows the following content of some of the rare earths and thorium:

| Y<br>ppm | La<br>ppm | Sm<br>ppm | Eu<br>ppm | Yb<br>ppm | Th<br>ppm |
|----------|-----------|-----------|-----------|-----------|-----------|
| 200      | 1700      | 400       | 50        | 40        | 3600      |



However, the major amount of rare earths occurs in the carbonatite of the dolomite-ankerite series where the rare earths also occur more coarse-grained than in the hematite rich portions of the deposit. An average analysis of such rock shows the following distribution of rare earths and thorium:

| Y<br>ppm | La<br>ppm | Ce<br>ppm | Pr<br>ppm | Nd<br>ppm | Sm<br>ppm | Eu<br>ppm | Gd<br>ppm | Dy<br>ppm | Th<br>ppm |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 183      | 3045      | 6475      | 883       | 1845      | 337       | 71        | 68        | 70        | 965       |

By mineralogical analysis and advanced mineral laboratory dressing methods the following rare earth minerals have been identified:

|            |   |
|------------|---|
| Parisite   | $2(\text{Ce, La, Di})\text{FCO}_3 \cdot \text{CaCO}_3$                  |
| Synchisite | $(\text{Ce, La, Di})\text{FCO}_3 \cdot \text{CaCO}_3$                   |
| Monazite   | $(\text{Ce, La, Y, Th})\text{PO}_4$                                     |
| Orthite    | $(\text{Ca, Ce, La})_2(\text{Al, Fe, Mg})_3(\text{SiO}_4)_3(\text{OH})$ |
| Kobeite    | $(\text{Y, Fe, U})(\text{Ti, Nb, Ta})_2(\text{O, OH})_6$                |
| Xenotime   | $\text{Y}(\text{PO}_4)$   |

and probably Fergusonite ( $\text{YNbO}_4$ ) and Bastnäsité  $(\text{Ce, La, Di})\text{FCO}_3$ , although the latter two are doubtful.

Considerable work and a number of methods, both physical mineral dressing and chemical and pyro-metallurgical treatments have been tried on materials from Fen in order to extract the rare earths from this the largest deposit known in Norway today. So far, however, these efforts have not been successful.

The main problem in Fen is the extremely fine grained and complex distribution of the minerals. In most parts of the deposit the grain size of the minerals containing rare earths is below 10 micron, although in certain special areas the grain size is considerably larger.

Mineralogical examination under the microscope reveals that some of the minerals show a very intertwined composition and a porous "coke-like" structure.

A very careful and tedious separation of the rare earth bearing minerals under the microscope has rendered minute samples of relatively clean fractions of specific minerals for further study.

The concentration of individual rare earth elements in the rare earth minerals orthite and synchisite, as well as in apatite and calcite concentrates from the above mentioned separation and in representative composite rock samples, have been determined by the flame emission method utilizing a nitrogen-shielded nitrous oxide-acetylene flame after chemical decomposition of the samples.

It has been demonstrated that the rare earth minerals have a much larger overweight of light (cerium group) rare earths than the representative rock samples. An apatite mineral concentrate (40% apatite) was found to contain more of the heavy rare earths than the representative composite sample.

The concentration of rare earths in the Fen apatite is very low ( $\approx 0,5\%$ ), and the apatite itself is rather scarce, so that this mineral cannot accommodate a significant proportion of the heavy rare earths.

Analysis of a calcite mineral fraction seems to indicate that the distribution of rare earths replacing calcium in this mineral is roughly the same as in the apatite. If this distribution is representative of the rare earth distribution in minerals other than orthite and synchisite, it may be estimated that the representative composite sample, contains up to 2% synchisite, and that this mineral, together with orthite, accounts for about 80% of the europium and about 40% of the yttrium present. An interesting feature of the Fen deposit is that the element europium obviously does not occur in the divalent state, because there is no europium "depletion" in any of the minerals or concentrates analysed.

The following table shows the content and distribution of rare earths in some of the minerals of the Fen deposit:

| %  | Synchisite   | Orthite     | Apatite concentrate | Calcite <sup>x</sup> | Whole rock |
|----|--------------|-------------|---------------------|----------------------|------------|
| La | 10.2         | 4.7         | 0.040               | -                    | 0.21       |
| Pr | 2.0          | 0.66        | -                   | -                    | 0.042      |
| Nd | 7.6          | 3.4         | 0.047               | 0.025                | 0.18       |
| Sm | 0.94         | 0.37        | 0.016               | -                    | 0.022      |
| Eu | 0.20         | 0.073       | 0.0045              | 0.007(?)             | 0.0052     |
| Dy | 0.15         | 0.04        | -                   | -                    | -          |
| Er | -            | -           | 0.006               | -                    | -          |
| Yb | 0.013        | 0.003       | 0.0032              | 0.004                | -          |
| Y  | 0.37         | 0.07 - 0.08 | 0.054               | 0.021                | 0.019      |
| Th | not detected | 0.16        | -                   | 0.08                 | -          |
| Ca | 10.6         | -           | 28                  | 35                   | -          |

x) Preliminary results.

At the company Elkems test station in Fiskaa Verk, Kristiansand, Elkem has run several smelting tests based on hematite from Fen and carbonate respectively. The purpose of these tests has been to study the distribution of the rare earths and thorium between the metal and the slag.

10 kgs of hematite of the following composition was smelted with 2.10 kg gas coke and 0.57 kg quartz in an electric smelting furnace of 50 kw capacity:

|   |       |
|---|-------|
| Fe  | 45,4% |
| SiO <sub>2</sub>  | 4,35% |
| CaO   | 10,6% |
| MgO   | 3,6%  |
| Al <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub> + P <sub>2</sub> O <sub>5</sub> + R <sub>2</sub> O <sub>3</sub> | 7,95% |

The test furnace was tapped 9 times and the average of the metal analyses gave the following result (from one of the campaigns):

Si 2,35%, Nb 0,08%, P 1,15%.

The slag from tapping No. 3, 4, 5, 7, 8 and 9 had the following composition:

|                                |       |                  |       |
|--------------------------------|-------|------------------|-------|
| SiO <sub>2</sub>               | 29,0% | TiO <sub>2</sub> | 0,30% |
| FeO                            | 0,77% | CaO              | 32,2% |
| Al <sub>2</sub> O <sub>3</sub> | 15,9% | MgO              | 10,7% |

and the distribution of the rare earths was as follows:

| Y<br>ppm | Ce<br>ppm | Sm<br>ppm | Eu<br>ppm | Gd<br>ppm | Nb<br>ppm | Th<br>ppm |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 870      | 26000     | 2200      | 290       | 460       | 70        | 20600     |

As will be seen the pig iron produced has a high content of phosphorous and a surprisingly low content of niobium. When comparing the rare earth analysis of the slag with the analysis of the hematite it appears that the rare earths and thorium have been concentrated approximately four times in the slag.

It has been tried to crystalize the slag by slow cooling in order, if possible, to obtain coarse crystals for further treatment by flotation etc. These efforts have not been successful.

### 3. RARE EARTH EXTRACTION

At an early stage it was decided to focus the attention on the production of yttrium oxide, leaving the other rare earths as alternative for later development. Thus, although some bench scale work has been performed on the separation and purification of samarium, europium and gadolinium oxides, the major part of the development work has been directed at processes for yttrium oxide production. The processes which the group has developed are now being tested on a semi-technical scale in a pilot plant designed for the production of 5000 kgs of yttrium oxide per year.

The pilot operation is at present based on xenotime concentrates, but in the course of the development programme, various other yttrium sources have also been tried. In the initial phase of the programme, the only rare earths containing materials immediately available to the project were some hundred kilograms of gadolinite and euxenite. These were by-products from small feldspar mines operating on pegmatites in the Evje district in Southern Norway. (Hand-picked minerals of this origin have quite a merit as raw materials for rare earth researchers; thus, some of the pioneering work of Dr. Spedding was carried out on the basis of Norwegian gadolinite from the same area).

### 3.1. Digestion

Opening of the minerals was mainly performed by acid digestion at elevated temperatures. In the case of gadolinite this is a straight-forward operation with any strong mineral acid. After some exploratory work, nitric acid digestion in batch type equipment was selected. The mineral was ground to 90% - 100 mesh, mixed with concentrated nitric acid in a ratio of 3 l of acid per kg of gadolinite, and heated to the boiling point. After filtering off the undissolved residue, excess acid was neutralized and the rare earths were recovered from the solution by oxalate precipitation and by solvent extraction methods.

Euxenite digestion was performed on a bench scale by boiling with concentrated sulfuric acid, or by heating to 350 - 400° C with ammonium sulfate or ammonium bisulfate. The effect of calcining the digested material at 650° C was also investigated. It was found that the main effect of this treatment was to render the uranium and thorium contents of the euxenite insoluble in water.

In one case, euxenite was used as raw material in the pilot plant. After being ground to -200 mesh and mixed with a xenotime concentrate, it was digested with sulfuric acid at 280° C. This experiment caused a variety of problems both in the digestion process and in the subsequent solvent extraction procedures, and after this experience, euxenite has been carefully avoided as a raw material for the pilot plant.

A rather extensive experimental programme of xenotime digestion was carried out. Both pure, hand-picked xenotime from Evje and the relatively lean Glamsland concentrates, containing from 1 to 5% yttrium oxide were used in these experiments. Digestion with concentrated sulfuric acid at 250 - 300° C was found to be the most convenient method. The normal procedure, which is easily applicable to pure xenotime or rich xenotime concentrates, consists in suspending the solids in a sufficient amount of acid to produce a slurry. This slurry is then heated in a stirred vessel to the desired temperature (usually 250° C) for an hour or two, which is sufficient to convert the rare earth phosphates to water soluble sulfates.

This "wet digestion" of xenotime is quite straight-forward apart from the corrosion and abrasion problems involved. The method cannot be employed with reasonable economy for the digestion of lean xenotime concentrates, however. The amount of sulfuric acid required to obtain a manageable slurry would far exceed the amount required for the actual digestion, and recovery of the excess acid does not appear practicable. Acid consumption by materials other than xenotime may also impair the economy.

For these reasons, a different digestion technique had to be developed for application to the Glamsland concentrates, which generally contain less than 10% of xenotime. Initial experiments showed that by using just enough acid to wet the solids, which is obtained at an acid: solids weight ratio of about 0.5 : 1, and heating to 300° C on a hot plate, digestion yields of yttrium of 80 - 90% were obtainable. This procedure, referred to as "dry digestion", was further developed and tested in various types of equipment on a small scale. This included rotary kilns and a rotating disc type furnace. In these cases the acid was first mixed into the concentrate and the resulting wet mass subsequently heated to 270 - 300° C. Since it is an obvious advantage to combine the mixing and heating in a single piece



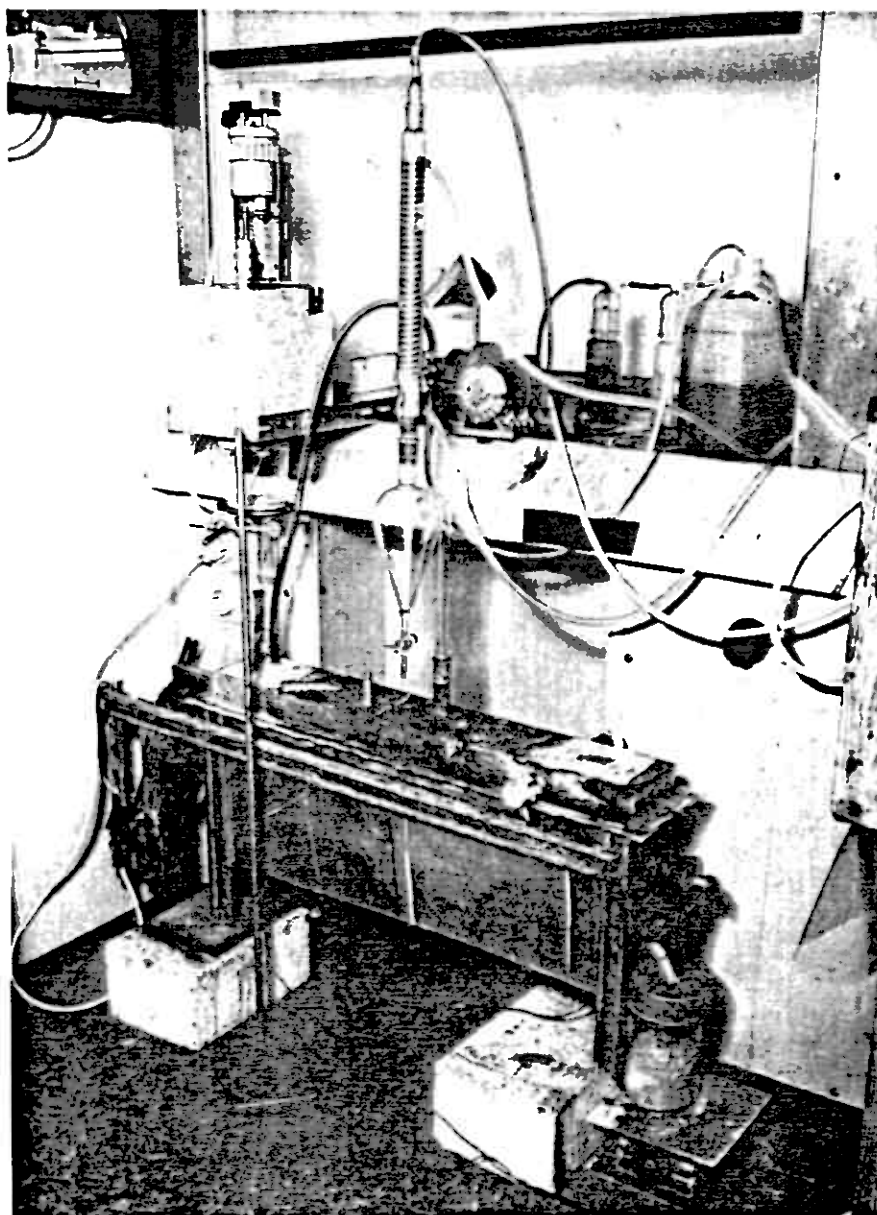


Figure No. 3. Lab.-scale version of "dry digestion" furnace.

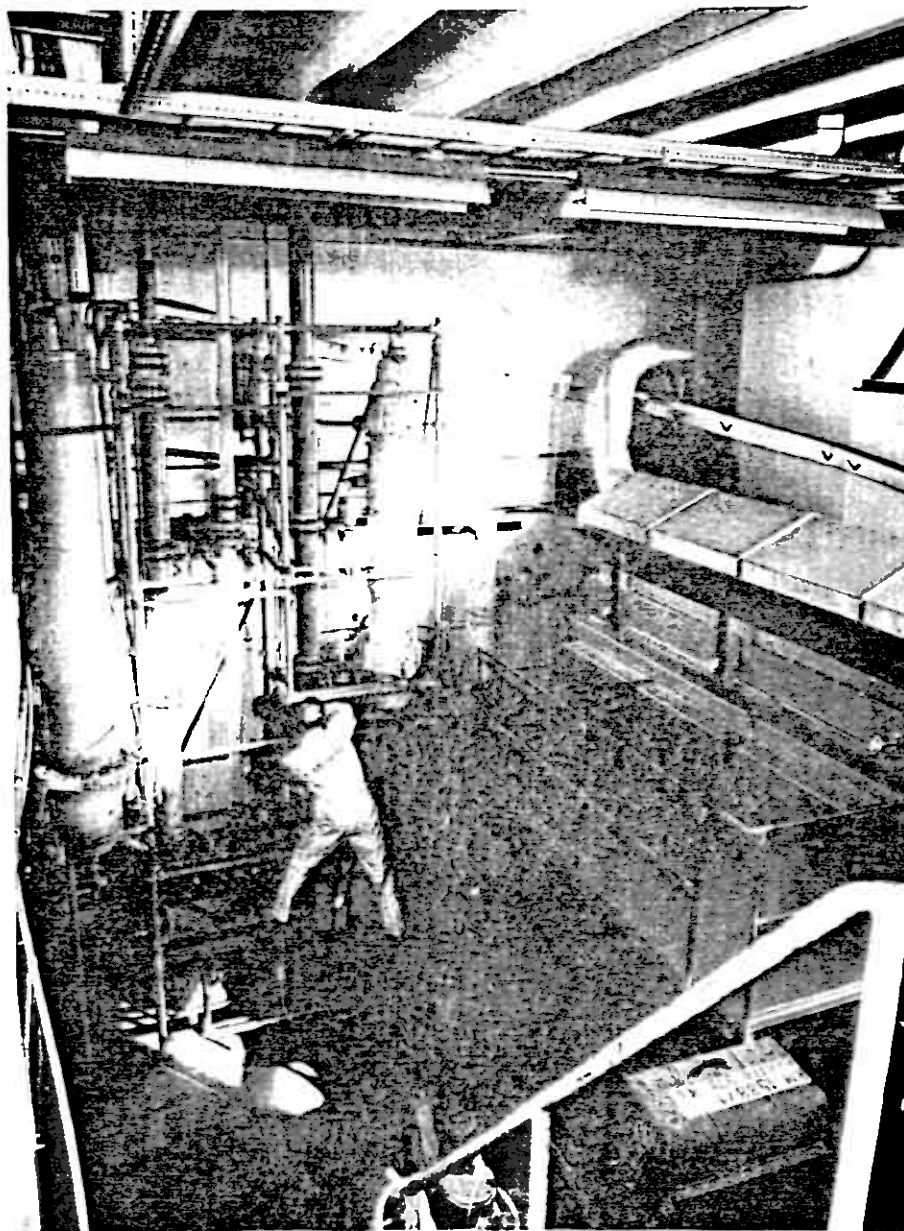


Figure No. 4. Pilot scale furnace with  $\text{SO}_3$  - recovery.

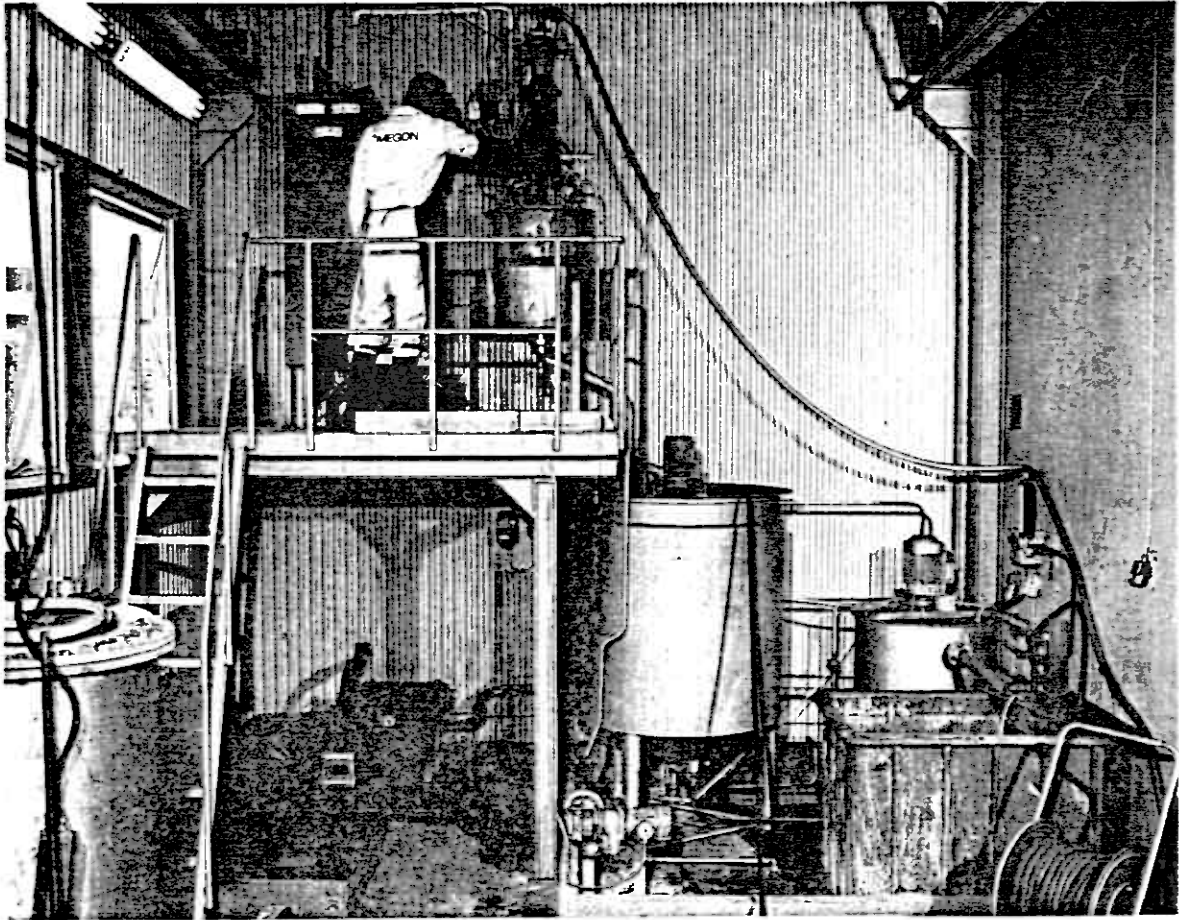


Figure No. 5. "Wet digestion" batch type equipment.



of equipment and operate this continuously, a special device was developed for this purpose. The lab. -scale version of the resulting furnace is shown in figure No. 3. Solids and acid are fed continuously into the furnace and are mixed and passed through it by means of rotating arms, mounted on a central horizontal shaft and equipped with scrapers. The semicircular trough of the furnace is heated by external, electrical heating elements.

"Dry digestion" of Glamsland xenotime concentrates in this lab. -scale furnace gave encouraging results, and a scaled-up version was designed and built for the pilot plant operation. This pilot scale furnace, designed for a throughput of 1 kg/min of concentrate, is shown in figure No. 4. It has been in operation for one year, and some of the operating experience is summarized below.

Material problems have been quite severe. The construction material of the furnace trough is an alloyed steel, "Sichromal" (Si: 1%, Al: 1%, Cr: 18%). This material stood up quite well against corrosion in the hot parts of the furnace, but corrosion was experienced in the "cold end" where the feed inlet and off-gas line connections are located. Corrosion in the off-gas line was severe, but it was reduced by external heating of the line. The parts most severely attacked, however, were the scrapers connected to the rotating arms. The concentrates used contain quite large proportions of quartz and garnet, and the abrasiveness of this material combined with the corrosiveness of concentrated sulfuric acid at 280°C, resulted in rapid deterioration of most of the materials tested in the scrapers. The only material found to be sufficiently resistant was "Kennametal", consisting mainly of tungsten carbide.

Distribution of acid within the furnace and the acid: solids ratio used were found to be critical parameters. Uneven acid distribution or a too high acid: solids ratio resulted in clogging. Once the furnace was shut down due to clogging, power failure or other reasons, the rotating arms stuck in the hard crust formed in the furnace. In order to resume operations it had to be cooled down and cleaned out.

The acid: solids ratio and the total amount of acid that could be fed to the furnace also seemed to be the limiting factors for the throughput obtainable. These values had to be limited to prevent clogging, and would thus limit the production rate obtained with a given yttrium content in the concentrate. Raising the yttrium concentration in the feed increased the production rate, as was demonstrated by adding richer xenotime concentrates to the Glamsland ore.

Although solutions were found to most of the problems described above, the main conclusion after one year of operating experience with the "dry digestion" furnace was that further operation was not justified in view of the high operating and maintenance costs involved. The furnace was therefore shut down this summer and replaced by the batch type equipment for "wet digestion" shown in figure No. 5. This change must also be seen in the context of a decision to use richer xenotime concentrates, purchased abroad, as raw materials in the pilot plant as a supplement to the Glamsland concentrates. These rich concentrates, containing 25 - 40% yttrium oxide are alternatively digested as such or used as addition to the Norwegian concentrates, since the raw material for "wet digestion" should contain at least 10% yttrium oxide to give a reasonable economy.



Digestion of other indigenous ores with potentials as rare earths raw materials has also been briefly investigated. Apatite from Ødegaarden has been dissolved in nitric acid, bringing its rare earth content quantitatively into solution, from where it could be recovered by partial neutralization. Treatment of the apatite with sulfuric acid, under conditions similar to those used in phosphoric acid production, transferred the rare earths to the liquid phase with yields of 70 - 80%. No attempts have been made to extract the rare earths from the phosphoric acid solution.

Sulfuric acid digestion of hematite from the Fen area gave acceptable yields (90% of yttrium present), similar results have been obtained with the slag from the smelting experiments described in the first part of this paper. However, the rare earth concentrations were too low and the acid consumption far too high to make this approach economically attractive. It seems that successful rare earth extraction from the Fen ores would depend upon a beneficiation method for upgrading the rare earth contents, and no such method has been developed so far. Thus, neither the Fen ores nor the Ødegaarden apatite are considered as practical raw materials for rare earth extraction yet.

After digestion of the xenotime follows water leaching in a stirred, cooled vessel. The undissolved residue is separated by sedimentation. For some time a centrifuge was used for this purpose, but the wear problems prevented its further use. It has now been replaced by a simple settling tank. The leach liquor is clarified on a rotary vacuum filter using a "Celite" precoat.

The yttrium content of the liquor ranges from 1 to 10 g/l, depending upon the concentrate used. The content of ferric iron in the leach liquor also varies with the type of raw materials used. With Glamsland concentrate, it may be as high as 10 g/l Fe(III). It is then necessary to incorporate a reduction step, since only limited amounts of Fe (III) can be tolerated in the subsequent solvent extraction step. (Fe(II) is not extracted and therefore does not interfere). By passing the liquor through a tower containing iron scrap (steel wool, turnings etc.) the Fe (III) is reduced to  $< 1$  g/l. Further reduction to  $< 0.1$  g/l may be achieved by means of sodium dithionite. This involves some disadvantages, however, due to sulfur dioxide formation and corrosion.

### 3.2. Solvent Extraction

After reduction and filtration, the leach liquor is adjusted for the solvent extraction step to follow. The purpose of this step is to separate yttrium from the major impurities in the solution, as well as from some of the lanthanides present. Yttrium is then also transferred from the original sulfuric - phosphoric acid solution to a nitric acid solution, which is more suitable for the subsequent purification steps.

The extractant is di(2-ethyl-hexyl) phosphoric acid (D2EHPA, dioctyl phosphate) in a 30% (volume) solution in a kerosene-type diluent (Shell-Sol T or TD). The extraction takes place in four box-type mixer-settler units. Some neodymium and all the heavier lanthanides are extracted together with the yttrium, while lanthanum, cerium and praseodymium remain in the raffinate. Four other mixer-settlers are used for re-extracting a fraction of the lanthanides, essentially



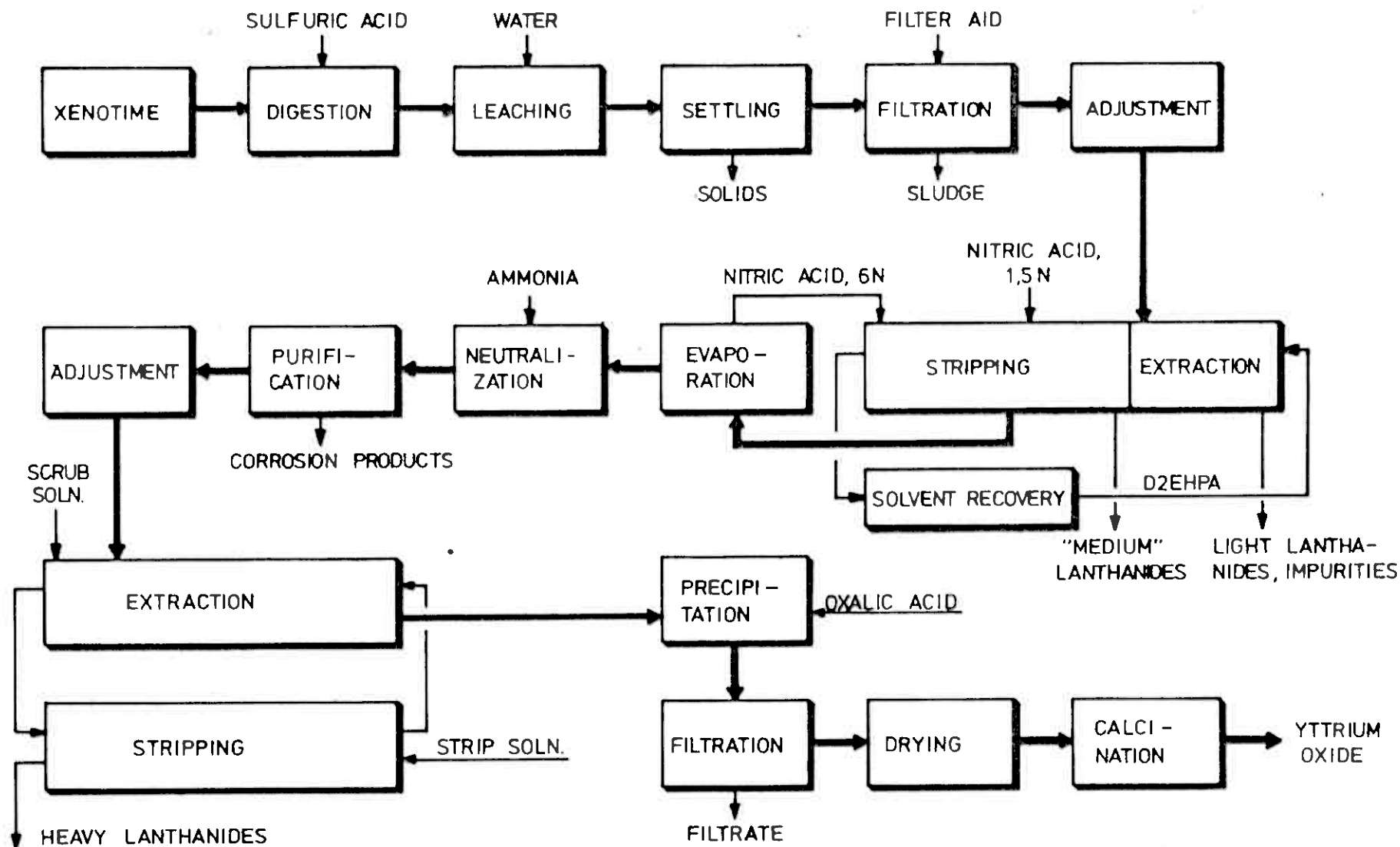


FIGURE 7. PROCESS FOR PRODUCTION OF HIGH PURITY YTTRIUM OXIDE.  
SIMPLIFIED FLOW DIAGRAM.

neodymium - terbium, with approximately 1.5 N nitric acid. This fraction contains samarium and gadolinium in significant proportions and is kept for further separation. Another purpose of this stripping operation is to remove traces of sulfuric and phosphoric acids from the organic extract prior to the final stripping. This takes place in an 8-stage mixer-settler, where yttrium and most of the heavy lanthanides are re-extracted with 6 N nitric acid. The strip solution is concentrated by evaporation to an yttrium concentration of 100 - 150 g/l, while 6 N nitric acid is distilled off and recycled to the stripping section.

The heaviest lanthanides (ytterbium, lutetium) are only partially stripped by the nitric acid, and require a separate stripping stage to prevent them from building up in the organic phase. Experimental work has shown that this may be accomplished with either 20% hydrofluoric acid or 50% sulfuric acid, but the final choice in the pilot plant was a 10% sodium hydroxide strip. Apart from the reduced corrosion problems, this has the advantage of removing other extracted species that are incompletely stripped by the nitric acid, e. g. ferric iron, thorium, etc.

After the caustic strip, the organic phase is re-acidified by contacting it with 1 N sulfuric acid in a 3-stage mixer-settler, and recycled to the extraction section. A flow diagram for the process is shown in figure No. 6.

Although some problems have occurred due to the formation of emulsions, "crud" and third phases (probably polymerized RE-D2EHPA), the D2EHPA extraction process has generally performed smoothly and satisfactorily. Emulsions have been avoided by operating at relatively high acidity (about 1 N), and third phase formation occurs only as a result from overloading the extractant. Losses of extractant with aqueous raffinates can be kept within reasonable limits, but diluent losses by vaporization have been fairly high.

The concentrated nitrate solution obtained in this step represents an intermediate yttrium product which is passed on for final purification. A typical rare earth distribution in such a solution is shown in Table No. I, which includes the distribution in the raw material for comparison. It is seen that the proportion of yttrium relative to other rare earths is increased from about 60% to about 75% by this process step.

The production of high purity yttrium oxide from this yttrium concentrate involves additional solvent extraction cycles for removal of the lanthanides as well as other impurities. The details of these process steps cannot be disclosed at present, except that quaternary ammonium compounds are used as extractants, and that yttrium is maintained in aqueous solution throughout the process, which is carried out in a completely continuous manner. Recovery of yttrium from the final product solution is by oxalate precipitation, followed by drying and calcination to yttrium oxide. A simplified overall process diagram is shown in figure No. 7.

An yttrium oxide product of high purity is obtained by this process. Total rare earth impurities are in the 1 - 10 ppm range, or, if one prefers to express it in terms of as many nines as possible: the quality is in the order of five to six nines. Typical analyses are given in Table No. II.



From the very beginning of the project, great emphasis has been laid on satisfying the analytical requirements. Development of efficient, rapid and accurate methods for rare earth analysis has been given high priority throughout the project. The analytical problems range from the determination of small amounts of rare earths and other elements in rock or mineral samples, through process analyses requiring speed and flexibility, to the accurate determination of trace impurities in the final product. "Classical" analytical methods are not of much use, and instrumental methods had to be developed and adapted to the various analytical tasks. Such methods include: X-ray fluorescence spectrometry, arc and spark emission spectrometry, flame emission and atomic absorption spectrophotometry, neutron activation analyses, and mass spectrometry. A variety of the latter method, employing isotopic dilution, has been found to be very useful for the accurate determination of the rare earth impurities in the yttrium oxide product.

Development work is under way for analytical methods which can be applied on line for process control purposes.

Simple methods for rapid evaluation of phosphors produced from the yttrium oxide made in the pilot plant have also been developed.

Finally, it should be mentioned that mathematical models of the processes employed in the pilot plant are being developed, permitting the use of process simulation as a valuable supplement to the actual pilot operation. The process simulation work has several objectives: to aid in the planning of experimental programmes for the pilot plant; to supplement the data obtained by the plant operation; to study the dynamic process behaviour and develop a suitable control strategy; and to serve as a tool for technical/economical optimization, process scale-up and feasibility studies of larger-scale projects. Such studies have been performed, and are currently being reviewed.

The pilot plant was ready for initial operation in the summer of 1970, but was modified for a new version of the final purification step in the beginning of this year. It resumed operation in April this year, and some hundreds of kilograms of yttrium oxide have been produced since then. Test marketing of this product is one objective of the project, apart from its main purpose which is to establish the technical basis for an industrial operation.

Some impressions from the plant are given in photos No. 4, 8 and 9.

The future operation of the pilot plant will largely depend upon the market development for yttrium oxide and other rare earth products. The plant could easily be adapted to process development for alternative products, should this be advised by market trends.

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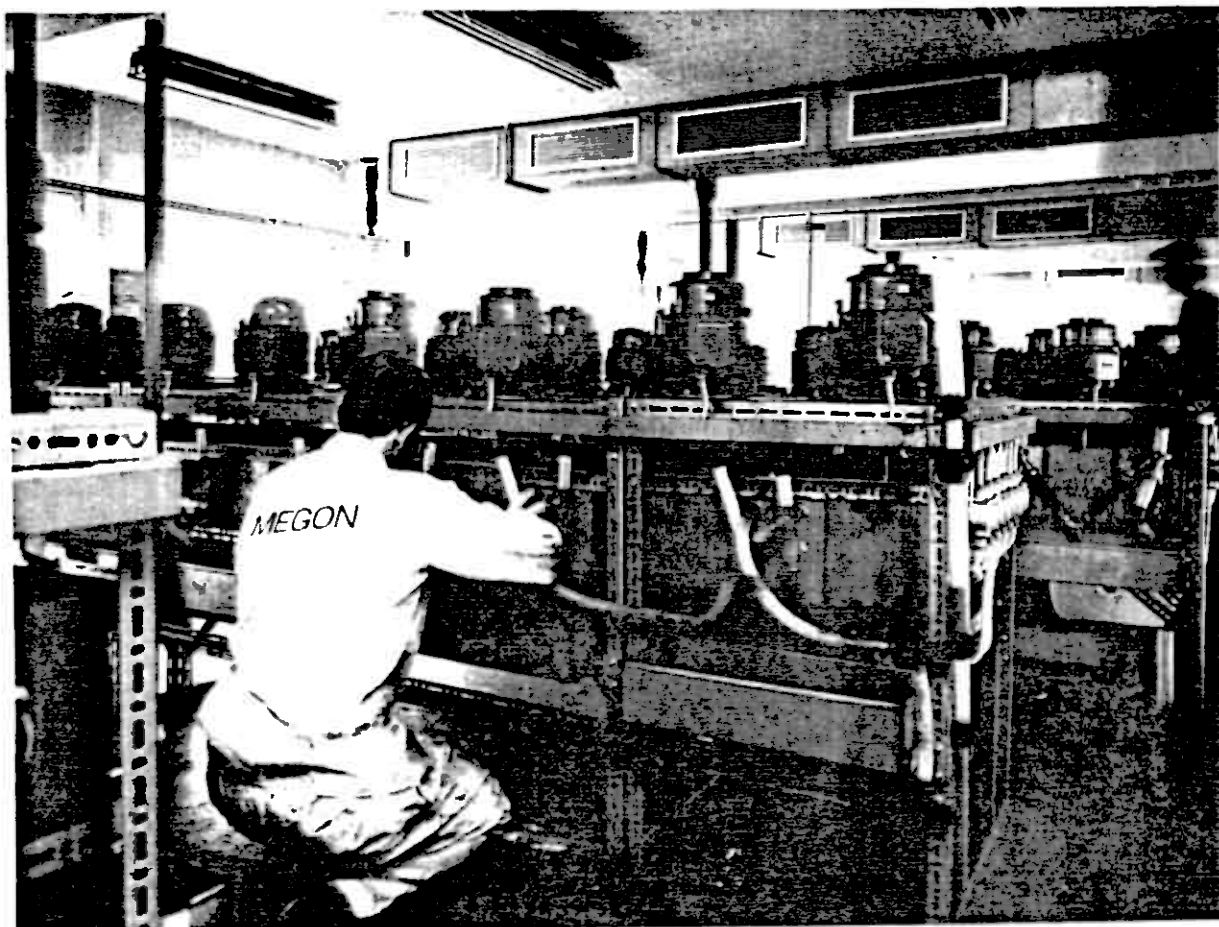


Figure No. 8. Mixer settlers in pilot plant.

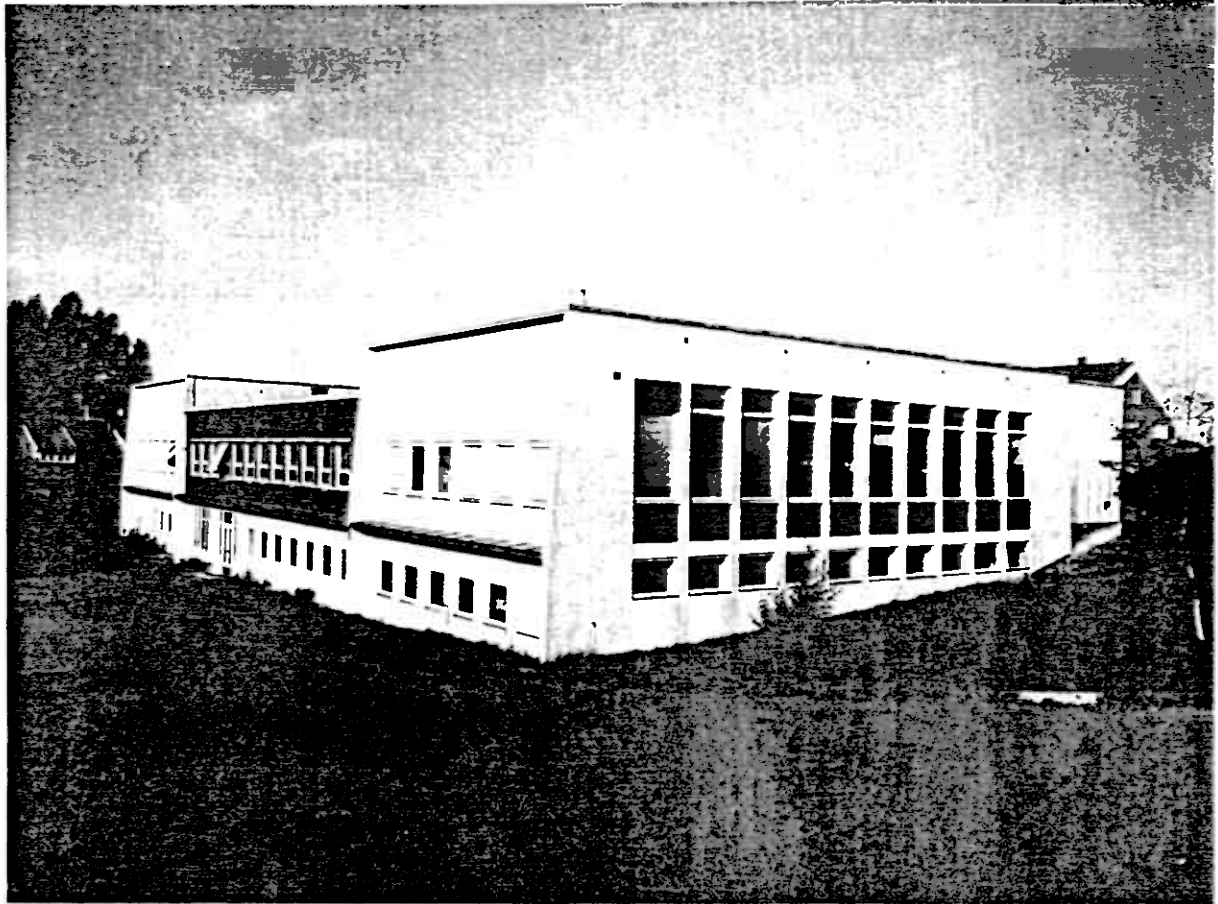


Figure No. 9. Pilot plant exterior.

TABLE I

Rare Earth distributions in intermediate product and raw material

| Element      | Conc. in inter-<br>mediate solution, g/l | % of total<br>Rare Earths | % of total RE's in<br>raw material |
|--------------|--|---------------------------|------------------------------------|
| Yttrium      | 174                                      | 75.2                      | 57.2                               |
| Ytterbium    | 12.5                                     | 5.4                       | 7.6                                |
| Thulium      | 2.0                                      | 0.9                       | (not determined)                   |
| Erbium       | 16.6                                     | 7.2                       | 7.7                                |
| Holmium      | 3.7                                      | 1.6                       | 1.9                                |
| Dysprosium   | 18.9                                     | 8.2                       | 8.3                                |
| Terbium      | 1.5                                      | 0.6                       | 1.1                                |
| Gadolinium   | 1.9                                      | 0.8                       | 3.4                                |
| Samarium     | -  | -                         | 1.3                                |
| Neodymium    | -  | -                         | 2.6                                |
| Praseodymium | -  | -                         | 0.6                                |
| Cerium       | -  | -                         | 6.2                                |
| Lanthanum    | -  | -                         | 1.9                                |



TABLE II

Analyses of high purity yttrium oxideMass spectrometric analysis of rare earth elements:

|    |       |     |    |     |     |
|----|-------|-----|----|-----|-----|
| La | < 1   | ppm | Tb | < 1 | ppm |
| Ce | < 1   | "   | Dy | < 1 | "   |
| Pr | < 1   | "   | Ho | < 1 | "   |
| Nd | < 1   | "   | Er | 3   | "   |
| Sm | < 1   | "   | Tm | < 1 | "   |
| Eu | < 0.1 | "   | Yb | 2.5 | "   |
| Gd | < 3   | "   |    |     |     |

Total rare earth oxides > 99.5%  $\pm$  0.5% (chemical analysis).

X-ray fluorescence and optical emission spectroscopy of other impurities:

|    |      |     |    |      |     |
|----|------|-----|----|------|-----|
| Ag | < 5  | ppm | Mo | < 10 | ppm |
| Al | < 20 | "   | Ni | < 10 | "   |
| Ca | < 10 | "   | Pb | < 50 | "   |
| Cr | < 10 | "   | S  | < 80 | "   |
| Cu | < 5  | "   | Si | < 50 | "   |
| Fe | < 10 | "   | Sn | < 50 | "   |
| Mg | 30   | "   | Ti | < 20 | "   |
| Mn | < 10 | "   |    |      |     |