THE SELECTION AND PERFORMANCE OF THE NATURAL ZEOLITE CLINOPTILOLITE IN BRITISH NUCLEAR FUELS' SITE ION EXCHANGE EFFLUENT PLANT, SIXEP

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ABSTRACT

SIXEP has been constructed by British Nuclear Fuels plc at its Sellafield reprocessing site as part of its commitment to reduce radioactive discharges to the Irish Sea. An extensive development program identified the natural ion exchange mineral clinoptilolite, from a particular deposit in California now owned by Tenneco Specialty Minerals, as the most suitable for use in SIXEP to extract caesium and strontium from spent nuclear fuel storage pond water. Close cooperation with the supplier in a Quality Assurance scheme ensured the supply of a fully-characterised, high grade ion exchanger. Since SIXEP commenced treating pond water on 28 May 1985, the plant has performed well, exceeding the design expectation in terms of discharge reduction and availability.

BACKGROUND

British Nuclear Fuels plc's (BNFL) site at Sellafield on the north west coast of England provides a spent nuclear fuel management service to the British and foreign nuclear power programs. Spent fuel delivered to Sellafield is stored for varying periods of time in large water-filled ponds before it is reprocessed to separate reusable fissile materials from radioactive wastes.

While water-filled ponds have proved to be an effective mode of spent fuel storage over a period of some thirty years at Sellafield, some corrosion of fuel has occurred, leading to the production of radioactive sludge and significant concentrations of radioactive ions in some storage ponds.

In the case of Magnox fuel (metallic uranium fuel clad with a magnesium/aluminum alloy), which has to date comprised most of the fuel from the British Nuclear Power Program, the amount of corrosion is limited as far as possible by maintaining the storage water at around pH 11.5, by dosing with sodium hydroxide, and by keeping the bulk water temperature as low as possible. In addition, the presence of non-radioactive ions in the water, which affect the corrosion of Magnox such as chloride, suplonate and silicate, is controlled to the lowest levels practic

The most significant products of the corrosion which does occur are caesium 137, caesium 134 and strontium 90, which are released directly to the pond water. A continuous, once-through, demineralised water purge is used to limit the concentrations of both radioactive and non-radioactive ions in each storage pond. These purges were discharged via a pipeline directly into the Irish Sea. Over the years different measures have been adopted to limit the quantity of radioactivity thus discharged to the sea, while at the same time controlling fuel corrosion rates and consequential radiation exposure to plant operators in the fuel storage ponds.

Discharge Reduction

In the late 1970's it was decided to construct a Site Ion Exchange Effluent Plant, referred to as SIXEP, to treat the various pond purges prior to discharge to the sea. SIXEP first began to treat radioactive pond water 28 May 1985 and has subsequently performed extremely well.

Among the interim measures introduced and steadily improved during the development, design and construction of SIXEP was a simple system of ion exchange skips. These skips were located in one of the fuel storage ponds through which pond water was recirculated until the ion exchanger could effect no further net absorption of activity. Fresh ion exchange skips then had to be introduced while the exhausted skips were sealed and retained in storage positions in the pond, positions which otherwise could have been used to store fuel.

Although cumbersome to operate, costly in terms of committed pond storage capacity, and limited in performance, these ion exchange skips, and associated measures, were successful. They maintained reasonably acceptable conditions in the storage pond and steadily reduced the site's discharges of caesium (and, to a lesser extent, strontium). As shown in Fig. 1, these discharges were reduced by a factor of about 10 over the nine-year period from the peak in the mid-1970's, a period when fuel stocks had increased substantially due to a number of coincident factors.

The availability of SIXEP: 1) has removed many of the previous onerous restrictions on the management of the fuel storage ponds necessitated by the interim control measures; 2) is leading to yet further reduction in the radioactive discharges from Sellafield and; 3) will assist greatly in future operations to clean up and eventually decommission the old ponds. The precise level of future discharges from Sellafield will, to a large extent, depend upon the performance of SIXEP in the longer term.

The SIXEP Process

The treatment process selected for use in SIXEP is shown in a simplified process flow diagram in Fig. 2. The main requirement is to extract caesium and strontium continuously from large columns of water (up to 3,900 M^3 (1.03 million gallons) per day). For this task a non-regenerable ion exchange process was

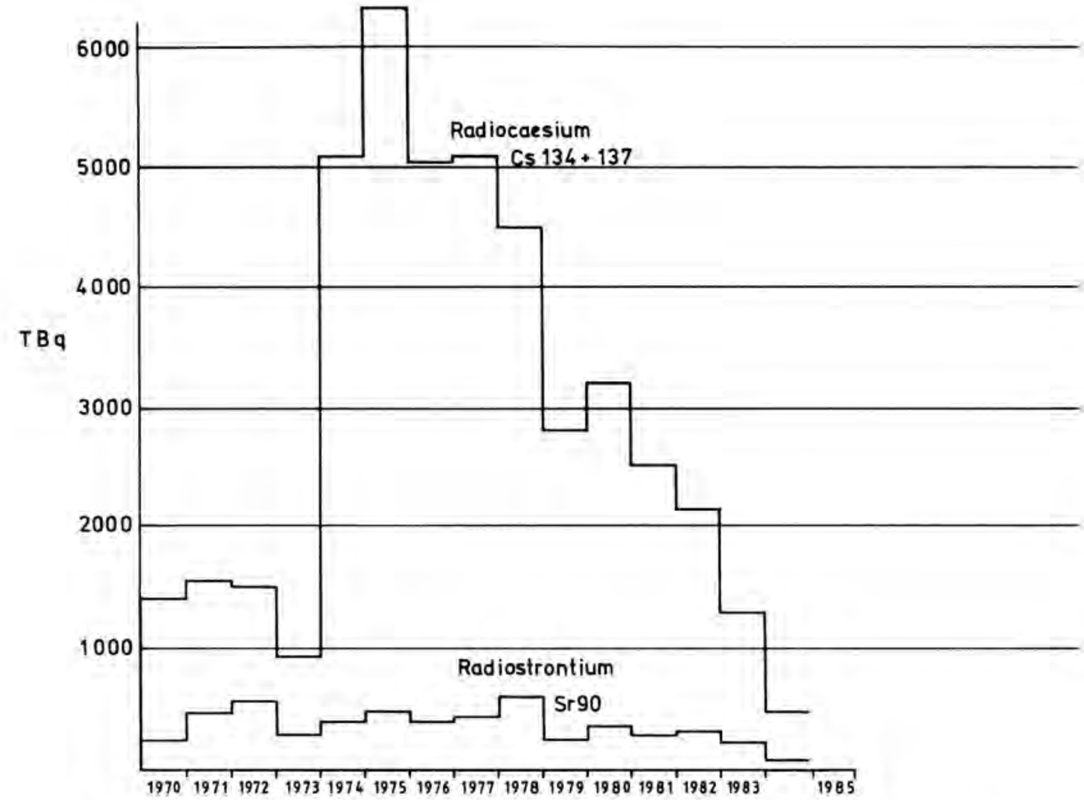

Fig. 1. Annual Discharges of Caesium and Strontium to Sea from Sellafield.

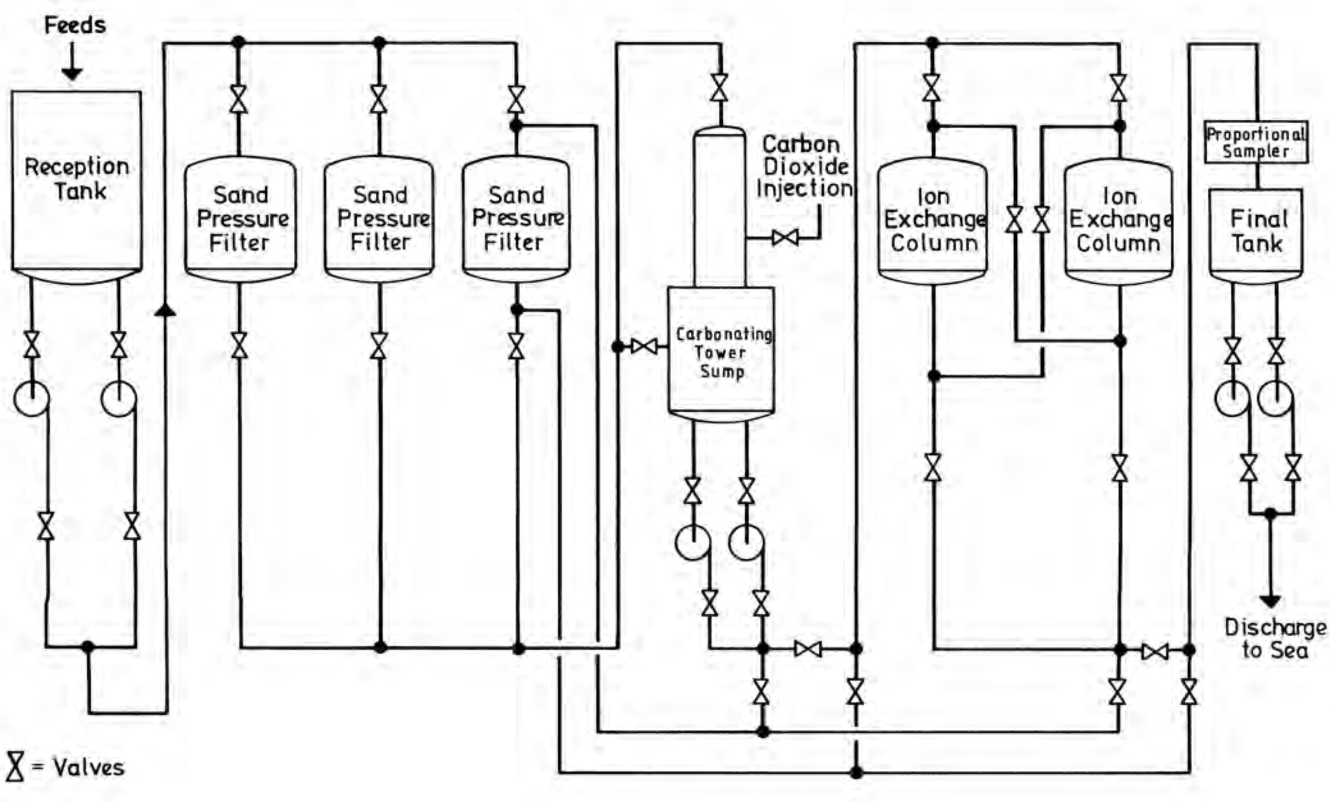

Fig. 2. The SIXEP Process.

selected with two ion exchange columns working in series. In order to optimise the performance of the ion exchanger, sand pressure filters (to remove fine particles of fuel corrosion sludge) and a carbonating tower (to condition the pond purges to around pH7) were also included in the process.

Four large storage tanks (nominally 1000 M^3 (264. 227 gallons) capacity each) are used to store spent ion exchanger, fuel corrosion sludge and any filter sand which can no longer be satisfactorily cleaned by the installed backwash system.

Selection of an Ion Exchanger

A major development program was initiated in the late 1970's to select a suitable ion exchange medium for SIXEP. The principal objective was to identify a material with a high selectivity for caesium and strontium in the presence of high concentrations of other feed constituents which may complete for ion exchange sites (Table I). Perferably the material needed also to be inorganic in order to provide a greater physical stability during subsequent storage and following eventual immobilization in the preferred encapsulating medium of concrete. Other factors, such as physical strength, were also of interest.

TABLE I

Typical Pond Purge Chemistry

CONSTITUENT		LEVEL
Sodium	100 ± 5	mg/l
Calcium	1.5 ± 0.1	mg/l
Magnesium	0.7 ± 0.01	mg/l
Caesium	2 ± 0.01	mg/l
Strontium	0.1 ± 0.01	mg/l
Silicate	10.0	mg/l
Chloride, Sulphate and Nitrate	5.0	mg/l
pH	11.5	

The development program included tests at laboratory scale and, for more promising materials, in a pilot plant using trace active simulants of the SIXEP feed.

Following a three year program the natural aluminosilicate zeolite clinoptilolite, from a particular deposit near Barstow, California was identified as being overall the best technical and economic option for SIXEP.

At that time (1980) the deposit of interest was owned by Occidental Minerals (OXYMIN), a subsidiary of Occidental Petroleum. Subsequently it has been acquired by Tenneco Specialty Minerals.

In negotiating with OXYMIN a supply contract for clinoptilolite two factors were of significance:

- The anticipated annual usage of SIXEP of clinoptilolite (50 - 100m^3 (1766 cu. ft. to 3532 cu. ft.) pa), although reasonably large in chemical plant terms was small in the context of economic mining. BNFL therefore opted to purchase the lifetime requirements of SIXEP at one time and store the material in drums in a BNFL warehouse close to Sellafield.

- While the chemical and physical characteristics of manufactured, synthetic, ion exchangers are well documented and predictably consistent, the same is not true of a natural material. A strategy of borehole sampling and Quality Assurance Tests was therefore developed in conjunction with OXYMIN.

Mining and Supply Strategy

The initial development program included borehole samples on a relatively coarse grid that identified the most promising area of deposit. In continuing the program, OXYMIN sunk a further series of boreholes on a closer (10.6m (134.8 foot)) grid in the best area. Testing of these core samples led to the selection of a supply which demonstrated not only acceptable and reasonably consistent properties, but which was also economically and technically feasible to mine. During the mining phase, the sample test results also provided sufficient detail to allow location and extraction of the rectangular slab of material selected from the clinoptilolite stratum. OXYMIN also agreed to segregate, as far as was practicable, the rock extracted from different areas and levels in the rectangular slab. Although this was an additional constraint requiring yet further care during mining operations, BNFL was interested in correlating different parts of the bulk supply with the detailed laboratory tests on the borehole samples.

The Quality Assurance scheme agreed, BNFL and OXYMIN identified a series of standardized tests, parameter acceptance levels and sampling frequencies. The tests, which included determination of total cation exchange capacity and physical properties (particle size distribution, bulk density, and moisture content), were performed on the sized product as it was loaded into the shipping drums.

While the tests were also chosen specifically for ease of operation "in the field", care was taken to correlate their results with the more stringent laboratory tests previously used to determine acceptable parameter levels for SIXEP.

The entire supply operation was completed over a period of about four months during which time BNFL inspectors monitored the material supplied by means of the Quality Assurance tests. As the bulk supply was delivered to the UK, samples were also taken for final confirmatory laboratory tests prior to use in SIXEP.

SIXEP'S PERFORMANCE

In the seven months since SIXEP commenced operation, the plant has performed significantly better than the design expectation, both in terms of discharges to sea and availability. During this time some 40,000m^3 (105.7 million gallons) of pond water have been treated, from which 4880 TBq of caesium have been extracted while caesium discharges to sea have only amounted to 5.6 TGq. This performance represents an average overall decontamination factor (df) for SIXEP to date of 370 compared with a design expectation of 150. The weekly availability of the plant to date has averaged 96 with a worst week performance of 72. In more recent weeks the plant's availability has been consistently close to 100. Clearly, more operating experience is required to establish the average df and plant availability for the longer term, but the early performance is encouraging.

The df achieved by SIXEP each week has varied as shown in Fig. 3 for caesium.

The initial steady improvement to a peak value of about 7000 reflected measures introduced to limit the rate of change of water flow through the clinoptilolite beds and a general setting down in the plant's performance. The subsequent decline to a minimum of 160 reflected the expected steady increase in breakthrough as the leading clinoptilolite bed proceeded towards saturation.

When, after four months' operation, the leading bed was emptied, replenished with fresh clinoptilolite and switched to the trailing position, the df subsequently developed along a similar pattern, except that the peak level achieved was somewhat lower at about 1700. As expected, the initial performance achieved with two completely fresh beds proved not to be representative of longer term performance for two main reasons:

- At a bed change the previously trailing bed which is switched to the lead position has already absorbed some caesium while in the trailing position. This mode of operation is adopted to maximize the utilization of the clinoptilolite absorption capacity, and thereby limit the volume of active ion exchanger requiring storage and, ultimately, disposal.

- Emptying the activity - loaded bed hydraulic transfer can never be 100% efficient, and small traces of material remain when the fresh bed is loaded. Activity is eluted from these traces as equilibrium conditions are re-established in the new bed.

The performance of SIXEP in extracting strontium from pond water fed for treatment in the plant has followed a similar pattern to that for caesium except the onset of strontium breakthrough from the leading bed occurs about a month in advance of that for caesium. Although strontium is of less radiological significance than caesium in discharges to sea, on-going investigations and operating experience in SIXEP will be seeking to establish the optimal balance between caesium discharges, strontium discharges and bed change frequencies.

CONCLUSION

BNFL is committed to using best practical means to reduce radioactive discharges from its Sellafield site to levels as low as can be reasonably achieved. The construction of SIXEP at the cost of 120 million pounds ($167 million) and the on-going optimisation of the plant's performance is an important part of the Company's overall strategy to achieve substantial reductions in its radioactive discharges to the Irish Sea. The performance of SIXEP to date indicated BNFL's significant investment in its extensive development program which led to the selection of clinoptilolite and the commitment with OXYMIN to ensure the supply of a fully characterized, high grade zeolite for SIXEP.

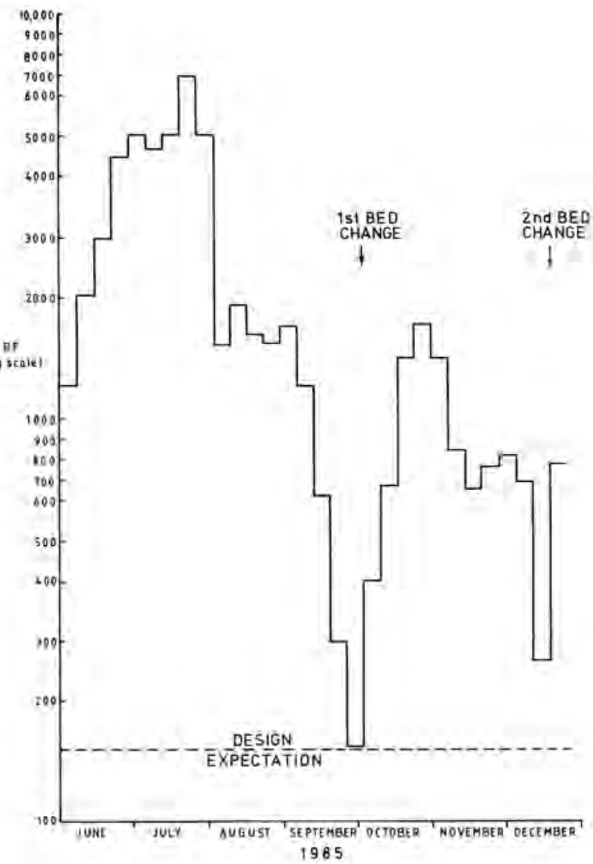

Fig. 3. SIXEP Early Operating Experience Weekly Caesium Decontamination Factor.

ADDENDUM

The overall building housing SIXEP is 102 meters long, 50 meters wide and 33 meters high. The plant incorporates some 40 km of stainless pipework and includes four 1000m3 tanks for storing radioactive solids arising from the treatment process and from the pond feeds. Control of the plant is highly automated involving some 1800 instrument loops. The pumps and valves used to pass radioactive water through the process are specially designed to allow removal and replacement of failed units.

ADDENDUM

The preceeding paper "The Selection and Performance of the Natural Zeolite Clinoptilolite in British Nuclear Fuel's Site Ion Exchange Effluent Plant, SIXEP", Mr. Baxter and Mr. Berghauser discuss the highly successful use of a clinoptilolite obtained from a deposit near Barstow California in reducing radioactive discharges into the Irish Sea. This particular clinoptilolite was selected only after an extensive search throughout the world to find the most suitable material for the task. Once the selection was made, techniques and capabilities were developed to mine and treat the clinoptilolite as a fine chemical feedstock for the SIXEP Project. The purpose of this breif paper is to point out those capabilities and the improvements made to them subsequent to the BNFL Project.

The deposit from which the subject material was obtained is the Mud Hills Mine of Tenneco Specialty Minerals located approximately 7 miles north of Barstow, CA. The quality of the Mud Hills deposit is extremely well characterized. It has been extensively drilled to locate the areas of highest quality within the deposit, and the highest quality areas drilled again on a 35 foot grid. The 3 inch diameter core from these holes was split and sampled at 1 foot intervals, with the samples being subjected to the testing program described in the paper. In addition to the direct characterization of the deposit, all available information has been used to generate a geostatistical model of the deposit that has proven highly accurate in subsequent operations.

As the basis of the mining plan used for the BNFL at Mud Hills, the high quality of the data permitted highly targeted mining of the deposit in 1 foot lifts within selected areas. The targeting of the mining, coupled with the segregation of clinoptilolite taken from the specific targeted areas, permits tailoring the material to very specific and exacting requirements.

The care taken in mining is, of course, contiuned into the milling, processing, and packaging of the Mud Hills Clinoptilolite. Careful monitoring of these processes assures that the product can be either extremely uniform in nature or can be tailored to specific needs. In the BNFL project, for instance, every 10th drum of product was sampled and tested for size consist, moisture content, bulk density, and cation exchange capacity. This care also extended into the final packaging of the material in shipping drums.

Tenneco Specialty Minerals Co. can now make available this system of production that will deliver to the most exacting specifications clinoptilolite of demonstrated proficiency.

Sea Discharge Treatment Cell Vessels & Pipework in SIXEP

Sample of Clinoptilolite rock and granules as used in SIXEP

The SIXEP Control Room

Upper Maintenance area of SIXEP

Lower Maintenance Corridor of SIXEP