

Demonstration Project for Seawater Purification Technologies

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1. INTRODUCTION

On March 24, 2014, the Mitsubishi Research Institute Inc. being the Project Management Office for the “Project of Decommissioning and Contaminated Water Management.” issued a RFP (Request for Proposal) for entities to receive subsidies and implement the “Validation of technologies for contaminated water management project” in the FY2013 Supplementary Budget. This project aims at improving the level of science and technology through the development of technologies that will be useful in decommissioning and contaminated water issues at TEPCO’s Fukushima Daiichi Nuclear Power Station.

The data and background material for this proposal have been downloaded from the website of the Mitsubishi Research Center:

In this proposal we present an approach based on 3 steps:

1. Electrokinetic removal of radionuclides from the seawater.
2. Collection of the radionuclides in a closed loop electrolyte system.
3. Removal of the radionuclides from the electrolytes by electrochemical ion exchange (EIX).

This electrokinetic and EIX technology and approach was developed primarily for the removal of heavy metals from soil and groundwater, but as is explained in this proposal can also be applied for seawater conditions.

2. BASIC CONCEPT

2.1 *Electrokinetic Technology*

Short History

Examination of the history of electrokinetics in soil will reveal it has its beginnings over 80 years ago. Some highlights are the work carried out by Puri and Anand (1936) who tested the value of applying an electric potential across a soil for removing sodium ions in order to improve the soil quality. Casagrande was the pioneer in stabilizing clays by electroosmosis and his attempts to remove water from lime sludge in the 1930s and 1940s. In the 1950s Collopy patented the use of electromigration for reclaiming saline soils. The beginning of the 1980s marked the interest both in Europe and in the USA of using the technology for the removal of toxic ions from the soil. Most of the early work and in particular the field experiments, however, were inconclusive due to the failure to manage the electrochemical changes in the soil around the electrodes. The breakthrough came in 1987 with Lageman, Pool and Seffinga from the Dutch company Geokinetics. They focused on electromigration and patented the use of circulating electrolytes around the electrodes and the use of ion permeable wells to manage and control the anolyte and catholyte. Since then Lageman c.s. have executed dozens of electrokinetic in-situ remediation projects in the Netherlands, Italy and the USA, recovering contaminants such as lead, copper, mercury, zinc, arsenic, cadmium, chromium, cyanides etc.

EKT and Radionuclides

Experiments with electrokinetic migration and removal of radioactivity from soil was carried out in the early 1990s by Pamuckcu et al., followed by Maes et al. at the turning of the millennium. The most recent studies on electrokinetic removal of radionuclides from the soil during the 2000s have been carried out by Kim et al. and Korolev et al., the latter mostly as a result of the accident at the Chernobyl Nuclear Power Plant in 1986.

2.2 Principle of electrokinetic remediation in soil

Electrokinetic soil and groundwater remediation methods are based on the transport processes that occur when an electric current is passed through the subsurface. The transport mechanisms of major importance to the electrochemical soil remediation methods are electromigration and electro osmosis. In the soil the current is carried by ions in the soil moisture or groundwater, and the anions (negative charged ions) will be transported toward the anode and the cations (positive charged ions) toward the cathode. This transport of ions in the electric field is electromigration. Electro osmosis is movement of pore water in the soil in the applied electric field.

The methods where an electric field is applied to a soil to remove chemical species are variably called e.g. electrokinetic remediation, electro-reclamation, electrokinetic extraction, electrokinetic soil processing, electrochemical decontamination or electrodialytic remediation.

The understanding of ion transport and ion mobilities, (that is, classical electrochemical phenomena) applies to the movement of ions in soil as it does in liquids, except for one major difference: ions interact with ion exchange sites on the soil and their progress is modified by this. Recovery of ionic contamination from ground is limited by the fact that soil is a powerful ion exchange media. Ionic contamination becomes adsorbed on soil particles following contact. Flushing alone will not recover it. A pH shift must be applied to desorb and mobilize it.

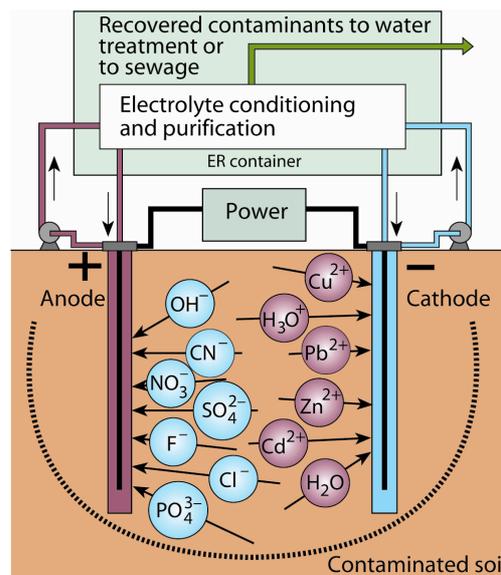


Figure 1. Schematic setup of electrokinetic system for in-situ remediation

2.3 Principle of electrokinetic remediation in seawater

When applying an electrical field in a liquid environment such as the seawater port at the Fukushima Daiichi Nuclear Plant, the ions in the seawater do not interact with ion exchange sites. Adsorption and desorption processes do not play any role in this respect. It means that there is no need for an electrolyte management system, which is used for maintaining an optimal pH of the anolyte and catholyte to control acidification and alkalinisation respectively. The electrolyte system will only be applied to collect the radionuclides and other ions out of the seawater and transport them to a treatment facility aboveground (figure 2).

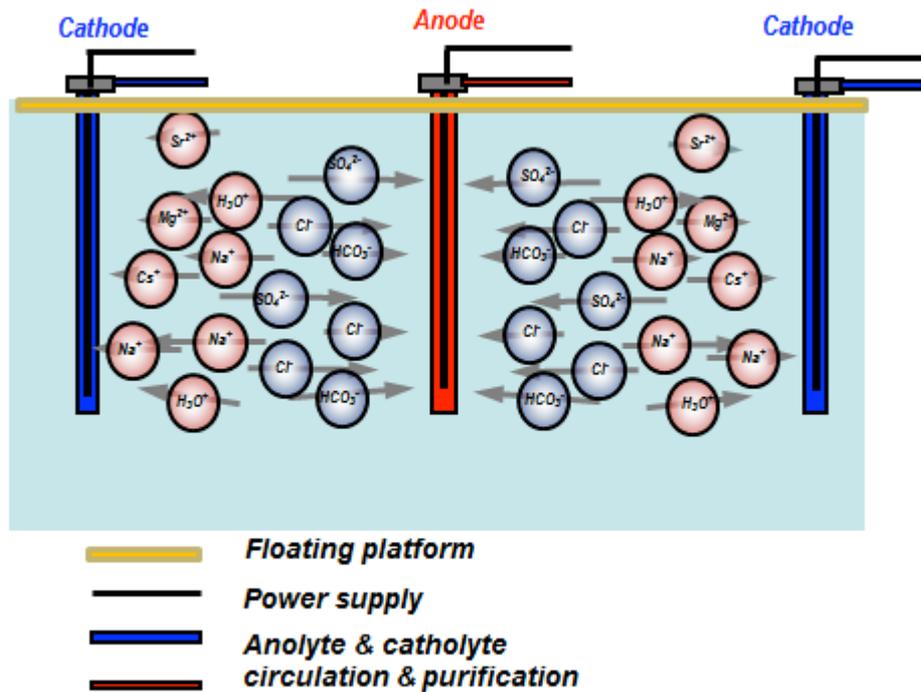


Figure 2 .Schematic setup of electrokinetic system in the FDNPS port

2.4. Principle of purification of electrolyte

As purification technology we are applying Electrochemical Ion Exchange (EIX). Originally EIX was developed to remove very low concentrations of radioactive materials and corrosive products from nuclear waste streams. The process has undergone considerable development. Various versions of EIX have been used to meet a wide variety of applications. Commercial units are in use in the following areas:

- Clean -up of nuclear fuel storage ponds.
- Removal of nitrate from drinking water.
- Clean-up process for heavy metals in plating rinse waters.
- Removal of radioactive iodine from hospital and pathology laboratory effluents.

EIX is simple in concept. Ion exchange media is attached directly on to an electrode surface. A counter electrode is placed opposite the media coated electrode and process fluids flow through the resulting chamber.

In operation, ions are adsorbed onto and then migrate into the media by the electric field gradient. Reversing the field polarity has the opposite effect, ions are driven out of the media. Figure 3 overleaf shows the key elements.

The diagram shows a cross section of the cell fitted with two cathodes coated with ion exchange media and two centrally mounted anodes.

Water to be treated enters the cell at the inlet. Metal ions (cations) are driven into the ion exchange media (in their attempt to reach the cathode) and occupy sites in the resin.

Periodic regeneration of the media is achieved by reversing the polarity of the electrodes. This drives the cations out as they attempt to reach the newly created cathode.

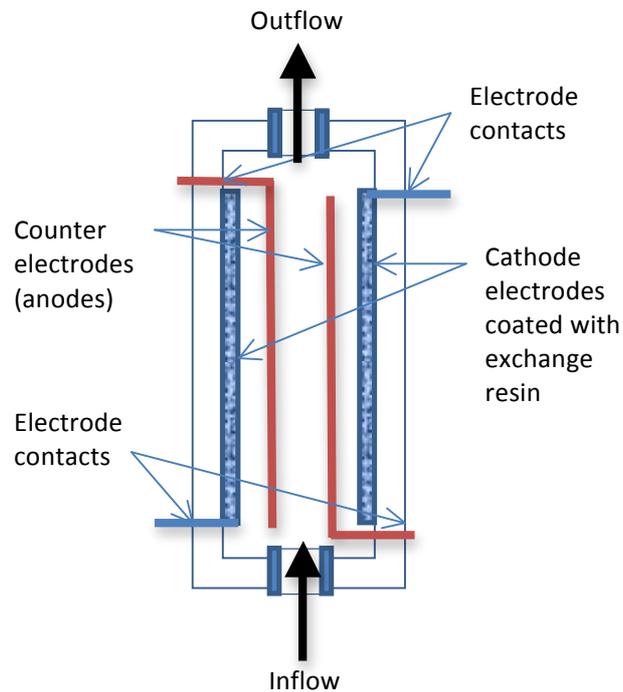


Figure 3. Principle of Electrochemical Ion Exchange

Regeneration can be performed in a single bed volume of water. Consequently the process can be used to recover concentrated and relatively pure solutions of captured ions.

The technology is extremely useful for operations in dilute solutions. It is not uncommon to reduce ionic concentrations from ppm to ppb. Electrochemical regeneration (using only the fluid within the cell) combined with the development of ion specific media, allows the process to be used to produce pure concentrated solutions from dilute complex ones.

EIX has several important benefits over traditional IX:

- Process kinetics are typically 10^3 greater than with IX columns, resulting in more compact equipment and lower capital costs.
- Utilization of the resin exchange capacity is as high as ions are driven in the resin matrix by electromigration.
- The open cell design avoids fouling commonly associated with packed bed IX. This is complemented by modular design and linear scalability.
- Elution can be performed in a single bed volume with no additional chemicals and high purity.
- Media can be considerably extended, as the electrochemical elution process is less stressful than the acid/base elution required for IX.
- Very high levels of selectivity are possible through electrochemical control of the process and careful media design.

The process works equally as well for anions. Alternatively, anions and cations can be treated in the same unit. Using this approach, EIX has been used to produce ultra pure water (>10W/cm) and to form concentrated salt solutions (>2M sodium nitrate).

The use of an electric potential in place of chemical reagents to elute ion-exchange media by ion migration, as well as perform redox and pH changing reactions is of considerable importance in simplifying subsequent recovery or disposal of the concentrate. The process has become known as Electrochemical Ion Exchange (EIX). EIX is an advanced ion-exchange process. Ion exchange media can be physically incorporated into an electrode structure with a binder. In the most basic system, this is in the form of a micro porous layer over which the waste to be treated flows. An electrical driving force is used to enhance absorption at the front face - giving removal factors > 1,000 if required up to high capacity utilisations of 75-100%. Through the choice of absorption media and the applied potential polarity, EIX systems have been shown to absorb cations of IA, IIA, transition and post-transition metals as well as anions. After the capacity has become fully loaded, polarity reversal can elute the ions without the use of regenerant chemicals back into a small volume - giving volume reduction factors of >1,000 and a concentrated product (>0.25M) suitable for subsequent immobilisation. The principles behind EIX technology are depicted in figure 3.

By making multiple and complete use of ion exchange capacity in this way, large volume reduction factors can be achieved for only <5% (depending on the feed concentration) of the energy required for evaporation. Selectivity is dependent on control of solution speciation by pH / valence adjustment combined with specific interactions with the selected absorber. This can be built into the operation of the EIX module by operating combinations of both cation (CEIX) and anion (AEIX) systems under independent current control. Due to the electrical driving force, the process is less sensitive to particulate fouling than conventional ion-exchange.

Absorption and elution processes can be combined into a single step - with continuous elution of a volume-reduced concentrate from the rear face of the electrode absorbing the contaminants from the waste stream. Selectivity is also possible by controlling the pH of the concentrate stream, enabling the separation of insoluble hydroxide species (e.g. Co) from soluble hydroxides (e.g. Na, Li).

Due to the intimate combination of high surface area absorbers with electrode structures, EIX can be used to treat both very dilute (>10 MΩ/cm) water and very concentrated salt solutions (>2M NaNO₃). The technique has also been combined with electro-kinetic techniques (primary treatment) to provide a total, integrated package of treatment technologies for soil decontamination and site clean-up.

An EIX prototype plant has been operational at the Doel Nuclear Power Facility in Belgium since 1993. Excellent results have been achieved operating the Doel rig on PWR low level waste (both primary coolant and floor drain wastes). The unit has routinely treated filtered waste from the PWR primary coolant reducing activity levels from 50 Bq/ml to <0.02 Bq/ml (DF of 2500) with a VRF> 1600, thereby, easily complying with the target for direct discharge to the environment.

The table below provides information on nuclear and industrial waste streams that have been successfully treated by EIX. In each case, the work has involved simulant testing for process evaluation and optimisation prior to plant build and deployment on real waste streams.

Waste	Cations	Anions
PWR	Cs, Co, Mn, Li	Cl ⁻ , SO ₄ ²⁻ , BO ₃ ³⁻
Fuel storage pond	Cs, Co	Cl ⁻ , SO ₄ ²⁻
Fuel fabrication	U, Pu	NO ₃ ⁻
Uranium mining	U, Ra	
Reprocessing	Cs, Sr	TcO ₄ ⁻
Water jetting, shielding	Cs, Co	
Resin decategorisation	Co, Mn, Ni	EDTA, citrate

Table1. Industrial waste streams treated with EIX

3. PRACTICAL IMPLEMENTATION

3.1 Location of test area

In order to demonstrate the effectiveness of our approach within the very short time span that has been allocated for the demo project, we have selected a test area of 80m x 10m x 4.5m at the northern end of the target area as indicated by MRI.

By choosing this location we avoid further outflow of radioactive species in the rest of the harbour, because the electrodes function as an electrokinetic fence. Furthermore, we can compare the status of the contaminant situation with that of the remainder of the target area at the end of the test period.

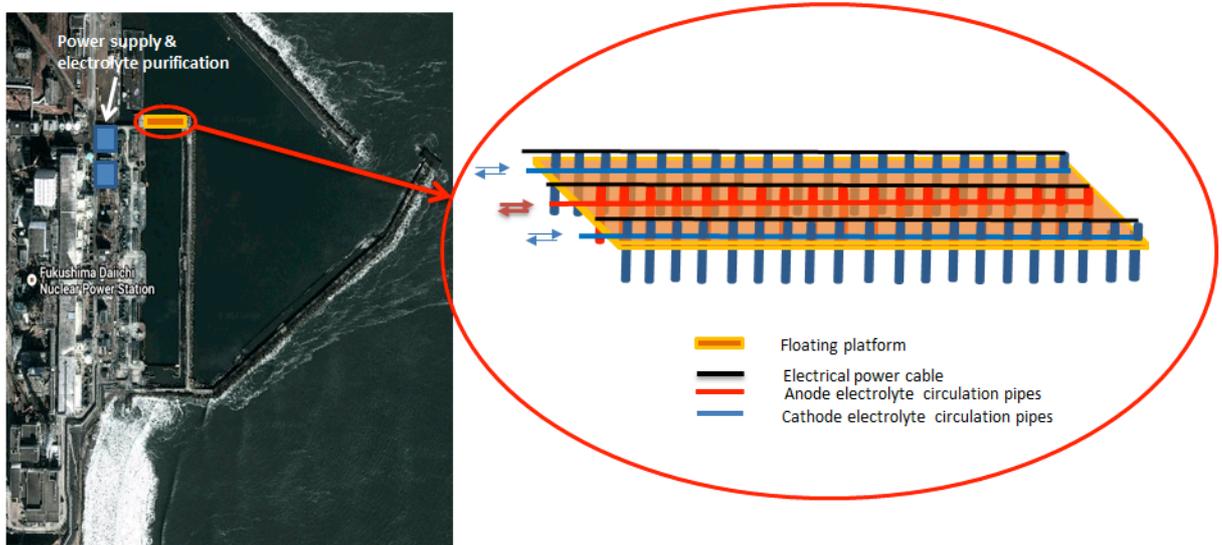


Figure 4. Demo site in target area with electrode series on floating platform

3.2 Configuration & set-up of the electrode system

The ion-permeable electrode casings will be installed on a floating platform, consisting of synthetic material (Each casing has a corrosion resistant electrode inside plus an inflow tube for the electrolytes (figure 5)). The electrode casings are placed along three lines, two anode lines on the outside with 21 anode-electrodes each and in between one cathode line with 21 electrodes, a total of 63 electrodes (figure 4). The electrodes are connected to a containerized power supply system on land.

The electrode casings are integrated in a centralized EIX-based electrolyte circulation and purification system (figure 5). Electrolyte is circulated in a closed loop between the electrode casings and the EIX units, which are built into a container on the land.

The distance between the anode and cathode lines will be 4m, while the mutual distance between the electrodes of equal charge will be also be 4m. The length of the electrode casings is 4.5m

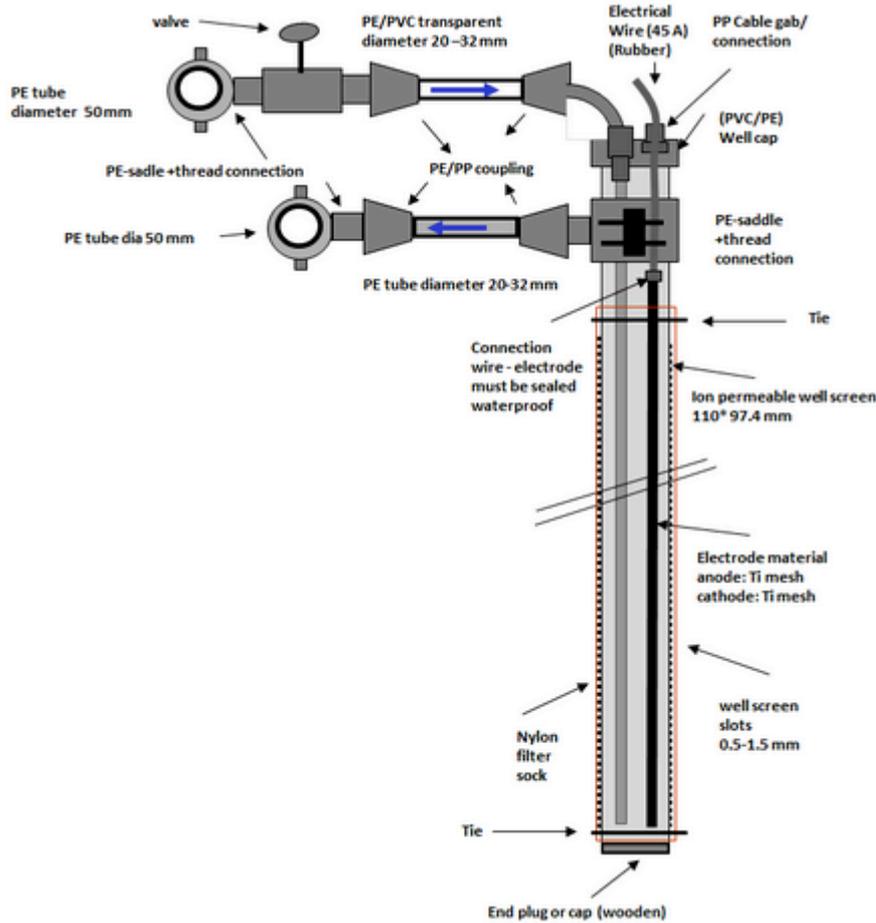


Figure 5. Electrode casing design with connection to circulation and electrical power system

3.3 Target for the amount of elimination

In the underlying table the present situation of the radioactive situation of the seawater in front of the cooling water intake is presented together with the maximum allowable concentrations required by law in Japan.

Item	Minimum	Maximum	Average	Max upper limit
Cs-137	10	34	27	90
Total β emission (Sr)	67	250	179	30
H-3	120	1000	492	?

Table 2. Radioactive composition of the seawater in the target area (Bq/l)

Based upon results with the EIX system our target for the demo test area will be at least the maximum allowable concentrations required by law in Japan.

3.4 Concepts of monitoring & maintenance

The process parameters are monitored automatically during remediation. Process data can be read out in real time by remote control. This is primarily in order to track the remediation process and if necessary make changes to it. The secondary intention is to determine whether the end result is

being achieved.

In case of breakdown, malfunctioning, or other trouble, an environmental technician has to be present and available for repairs and solve the problem. He also takes sea water and electrolyte samples. In principle one

Although most of the process parameters are monitored automatically, there are process parameters that need to be collected and sampled by hand or that have to be measured in case of malfunctioning of the equipment. Moreover the field equipment is located in a corrosive environment and needs regular control. Therefore, at the start of the demo project a monitoring plan will be presented. The intention of the monitoring plan is to make clear to the operator / technician which process parameters need to be collected and sampled and with what frequency and which parts of the equipment need to be checked regularly.

The monitoring plan needs to be updated regularly so as to ensure that monitoring is effective. The plan usually consists of a block diagram setting out the action to be taken and the time. The standard unit of time is one week. The plan covers the following items:

Power supply: Checking of overall operation of power supply. Checking connection between electrical cables and electrodes on the platform. These parameters are basically checked and noted during every visit to the site.

Electrolyte circulation system: Clean and calibrate measurement electrodes, check circulation of cathode and anode electrolytes and operation of pumps, alarms, valves, and shut-off devices and connection of pipes and ducts to the electrode casings.

Electrolyte purification system (EIX): Clean and calibrate measurement electrodes. **Influent:** Sampling of the electrolyte at the inflow of the EIX system. The frequency of sampling and the number of samples taken will be established at the start of the demo project. The plan also indicates what features are to be analysed and the type of sampling to be used. **Effluent:** Sampling of the electrolyte at the outflow of the EIX system.

3.5 Personnel

For daily control and periodic maintenance of the test demo, one operator and one technician is needed.

3.6 Concepts for secondary wastes

The basic concept of our proposed technology is to capture ions out of the seawater in an electrolyte. The consequence thereof is that no seawater is pumped and no large volumes of water have to be treated, but only the electrolyte fluid.

Secondary waste will consist of natural sea salt which can be returned to the sea and a concentrated solution of radionuclides. In this demo project the total volume of the electrolyte fluid is approximately 0.6 m³. The electrolyte is circulated at about 1 m³ per hour.

4 ELIMINATION EFFICIENCY

4.1 Description

Electrokinetic remediation of soils during the past 20 years resulted in clean-up efficiencies varying between 60 and > 90%. In this respect it should be once more noted that soil is a strong exchange media and ion mobilities are greatly affected by this. It results in much lower ion velocities. These can only be increased by increasing the potential drop between the electrodes. In seawater the radionuclides will have to compete with the abundantly present Cl⁻ and Na⁺ and SO₄²⁻ ions.

Regards EIX, an EIX plant has been operational at the Doel Nuclear Power Facility in Belgium since 1993. Excellent results have been achieved operating the Doel rig on PWR low level waste (both primary coolant and floor drain wastes). The unit has routinely treated filtered waste from the PWR primary coolant reducing activity levels from 50 Bq/ml to <0.02 Bq/ml (DF of 2500) with a VRF > 1600, thereby, easily complying with the target for direct discharge to the environment.

Decommissioning waste streams have been successfully treated at throughputs of around 0.75 m³/h per m² of EIX membrane electrode area to give Cs and Co DF's of 1000 and VRFs > 5000.

4.2 Sustainability of elimination effects

Electrokinetic scale-up is based on extending the platform area and installing more electrodes. The consequence hereof is that power supply, electrolyte circulation and purification have to be scaled up. This can be easily accomplished, as the electrokinetic system is modular and it only needs additional modules to be added.

EIX plant scale-up is based on manifold parallel flat plate modules. It is simple in both construction and operation - being remotely and automatically controlled - thus reducing operator dose. It operates at ambient temperature and pressure. There are minimal reagent additions, thus reducing waste volumes and hence waste disposal costs. Due to the intensified nature of the process combined with selectivity, the plants are both compact and energy efficient. The plant can be decategorised to LLW/free release prior to disposal.

4.3 Suppression of secondary waste generation

As explained before, the secondary waste consists of a small volume of concentrated solution of radionuclides. This waste has to be dealt with according to standing procedures and regulations.

4.4 Duration of purification

We have calculated a time period of about one year to purify the test area with a seawater volume of 4000 m³.

For the total target area with a seawater volume of approximately 160,000 m³ we estimate a period of 3 years to remove the radionuclides.

4.5 Energy consumption

The energy consumption of both the electrokinetic and EIX systems are in the order of 50 kWh/m³ of seawater.

5 COST

As we have kept this proposal outside competition, we refrain from giving a detailed cost estimate, but it may be indicated that it is substantially lower than the maximum subsidy amount of 400 million Yen.

The fact that no large volumes of seawater have to be pumped and only a relatively small volume of electrolyte has to be purified, will lead to a considerable cost reduction as compared to other techniques.

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