

Method for detection of radionuclide in seawater prior to water reclamation into drinking water

This invention relates to a detection method for measuring seawater for one or more radionuclide and diverting the seawater for electro-coagulation to aid in the removal of suspended and dissolved radionuclide material.

Background of the present invention

Sea water is slightly radioactive: it contains a small but significant amount of radioactive elements that undergo spontaneous radioactive decay and produce energy, subatomic particles, and a remainder, or daughter nucleus, smaller than the original. The particles include alpha particles (two neutrons plus two protons), beta particles (electrons), and gamma energy. The radioactive elements are called radioactive isotopes, or radionuclides, or nuclides. Nearly all of the radioactive material in the ocean is natural, and represents material that has been on Earth since its formation

Human beings have been concentrating, creating, and using radionuclides for a century, and have added to the inventory of natural radionuclides, although the amount added is small compared to natural amounts. Among the important artificial nuclides are tritium, (^3H), ^{131}I , ^{129}I , ^{137}Cs , ^{90}Sr , ^{99}Tc , and ^{239}Pu . Weapons testing and waste from nuclear reactors are two of the main sources from which these nuclides may enter the ocean, in both cases through its surface waters. In addition, disposal of nuclear waste such as submarine reactors in the ocean has created point sources of the material on the sea floor

U is quite soluble in sea water, Th is nearly totally insoluble, Ra is soluble, and Rn is a noble gas that is soluble in water and can escape into the atmosphere. As long as all the members of the ^{238}U decay series are kept in a closed container, they will eventually reach the state where they all are decaying with the same number of decays per second, because the half-life of the first decay is so long relative to subsequent decays. This state is called secular equilibrium, and will continue indefinitely unless some of the material escapes the container, or extra material is added

The ^{230}Th daughter has a long half-life (75,300 years); it is also the chemical element thorium, and sticks to particles falling through the ocean, whereas its parent ^{234}U stays dissolved in sea water. The long half-life allows excess ^{230}Th to build up in sea-floor sediment, with very high values at the surface and decreasing amounts in the older sediment at depth.

The change with depth results from the decay of ^{230}Th over the thousands of years required for a few centimeters of marine sediment to accumulate. The change in ^{230}Th with depth in the sediment, plus knowledge of the ^{230}Th half-life, makes it possible to use the information to calculate the deposition rate of sediments on the seafloor

The artificial nuclides in the ocean have originated as global atmospheric fallout resulting from nuclear weapons tests, or from point sources derived from nuclear reactor wastes entering the ocean, or from nuclear accidents. * The atmospheric fallout has a well-known history.

Atmospheric weapons tests began in the early 1950s, and continued until 1962 when the atmospheric nuclear test ban treaty was signed by most of the countries that had been conducting the tests. The treaty was prompted by the alarming spread of the radioactive contaminants into the environment and even into the human food supply. ^{90}Sr was easily detectable in milk, for example. After the test ban, the levels of fallout nuclides decreased abruptly.

One of the products of nuclear weapons testing was tritium. Its distribution in the ocean is like a telltale ink stain revealing the history of its occurrence on Earth. Tritium entered the ocean at the surface and became involved in the sinking North Atlantic water, part of the thermohaline current system that circulates ocean deep water. As the North Atlantic Deep Water moved downward, so did the tritium. Its concentration at various depths and locations gives a picture of a current system at work.

Chernobyl

Chernobyl reactor accident, which occurred in 1986. The reactor released a plume of radioactive contaminants that changed direction over a few weeks and contributed measurable radioactivity over

Europe, Scandinavia, North America, and Russia. The danger in such contamination results from the very high concentrations found in local areas. Additional sources of nuclear contamination from nuclear waste disposal and spills by the former Soviet Union have added a very large amount of radioactivity to the Arctic Ocean

Fukushima Daiichi

The 2011 Tōhoku earthquake and tsunami was a 9.0-magnitude undersea megathrust earthquake off the coast of Japan that occurred at 14:46 JST (05:46 UTC) on Friday 11 March 2011. The epicenter was approximately 72 kilometers (45 mi) east of the Oshika Peninsula of Tōhoku, with the hypocenter at an underwater depth of approximately 32 km (19.9 mi).

The earthquake triggered extremely destructive tsunami waves of up to 23.6 m (77 ft) that struck Japan minutes after the quake, in some cases traveling up to 10 km (6 mi) inland, with smaller waves reaching many other countries after several hours. Tsunami warnings were issued and evacuations ordered along Japan's Pacific coast and at least 20 other countries, including the entire Pacific coast of North America and South America

Officials from the Japanese Nuclear and Industrial Safety Agency have reported that radiation levels inside the plant are up to 1,000 times normal levels, reactor 3 runs on mixed uranium and plutonium oxide, or MOX fuel, making it potentially more dangerous in an incident due to the neutronic effects of plutonium on the reactor and the carcinogenic effects in the event of release to the environment.

US Navy relief group moved from the immediate area after its helicopters detected low-level radiation while returning to their aircraft carrier from a search and rescue mission, 160 km (99 mi) offshore. The flight absorbed the equivalent amount of earthbound background radiation for a month in the span of about an hour. It was reported that radioactive iodine was detected in the tap water in Fukushima, Toshigi, Gunma, Tokyo, Chiba, Saitama, and Niigata, and radioactive cesium in the tap water in Fukushima, Tochigi and Gunma.

At the time of the accident, reactor No. 1 contained 400 fuel assemblies, No. 2, No. 3, and No. 5 548 fuel assemblies, and No. 6 764 fuel assemblies in their respective reactors. Reactor No. 4 was empty of fuel assemblies in its reactor, but had 1,331 spent fuel assemblies in its cooling pool. Reactor No. 1 had 292, No. 2 587, No. 3 514, No. 5 946, and No. 6 876 spent fuel assemblies in their respective cooling pools. A decay heat output of 7 MW (typical of a Fukushima reactor a few days after shutdown) has the capacity to boil off about 200-300 tonnes of water per day, which puts the requirement for cooling water in context.

The move by Tokyo Electric Power Co. (TEPCO), which operates Daiichi, to use seawater doped with neutron-absorbing boron in the reactors' pressure vessels all but ensures that they will never function properly again, permanently damaging one of the world's 25 largest nuclear power stations. TEPCO started seawater cooling at 20:20, adding boric acid as a neutron absorber to prevent a criticality accident, these conditions resulted in unsafe levels of radioactive contamination in the air, in drinking water, and on certain crops in the vicinity of the plant.

The Japanese Ministry of Health, Labour and Welfare announced that levels of radioactivity exceeding legal limits had been detected in milk produced in the Fukushima area and in certain vegetables in Ibaraki. Measurements made by Japan in a number of locations have shown the presence of radionuclides on the ground. On March 23, Tokyo drinking water exceeded the safe level for infants, prompting the government to distribute bottled water to families with infants. World wide measurements of wind-born radioactive iodine and caesium vented from reactors suggest that levels have reached around 2/3 those during the Chernobyl disaster.

Radioactive iodine, caesium, ruthenium, and tellurium were detected in seawater samples in the vicinity of the station on 23 March, and radioactive iodine and ruthenium have been detected in seawater samples 16km from the power station.

Based on extrapolations made on the mean temperature and tonnage of seawater utilized for the "last ditch" attempt to moderate the reactor core, spent fuel pool, significant contamination of seawater not entrapped within the cooling pond of the nuclear reactor facility would have picked up various

radionuclide from a number of pathways, ranging from direct contact contamination to ion-to-ion irradiation.

In one study, "EFFECT OF SEAWATER LEVEL ON CORROSION BEHAVIOR OF DIFFERENT ALLOYS" Saleh A. Al-Fozan and Anees U. Malik, Saline Water Desalination Research Institute, the corrosivity of the seawater is reflected by the fact that most of the common structural metals and alloys are attacked by this liquid or its surrounding environments.

Oxygen, biological activities, pollution, temperature, salinity and velocity are the major factors which affected the corrosion behavior of materials, for carbon steel, the corrosion product will be built up on the surface which would reduce the mass transfer of oxygen and other agents to the metal surface resulting in the reduction of the kinetic of the cathodic reactions.

The above study is notable since various steel alloys were tested in different submersion levels of sample seawater at a fairly consistent test temperature. Under the extreme conditions experienced at the Fukushima nuclear reactor plant, with the added complication of high radioactivity beyond its intended design range due to the complete breakdown of coolant to control its residual fission heat, the potential for a wide range of contamination with the various trace elements present in seawater is considerably higher.

Novel radionuclide contamination route in seawater

Ballast water contamination of coastal cities: In order to maintain stability during transit along coasts and on the open ocean, ships fill their ballast tanks with water. Large ships often carry millions of gallons of ballast water. This water is taken from coastal port areas and transported with the ship to the next port of call where the water may be discharged or exchanged.

The ballast water of shipping vessels has been a primary method of alien species introduction throughout the world. Scientists estimate that as many as 3,000 alien species per day are transported in ships around the world, however, not all transported species survive the trip and their new home. Some of the species that do survive the trip are able to thrive in their new environment. These bioinvaders can cause disruptions in the natural ecosystem, economic troubles, and even carry human diseases.

According to the IMO, the problem of invasive species in ships' ballast water is largely due to the expanded trade and traffic volume over the last few decades and since the volumes of seaborne trade continue to increase the problem may not yet have reached its peak. The effects in many areas of the world have been devastating. Quantitative data show the rate of bio-invasions is continuing to increase at an alarming rate and new areas are being invaded all the time.

A table of the various radionuclide found in the seawater surrounding the Fukushima Daiichi nuclear power plant indicates the following:

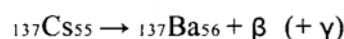
Caesium 137
Caesium 134
Caesium 136
Iodine-131

While the half-life of Iodine-131 is 8.02 days, Caesium has a half-life of 30.17 years.

Isotope	Decay constant (Year-1), (day-1)		Half-life (year), (day)	
Rubidium (^{87}Rb)	1.46×10^{-11}	4.00×10^{-14}	4.75×10^{10}	1.73×10^{13}
Uranium (^{238}U)	1.55×10^{-10}	4.24×10^{-13}	4.468×10^9	1.63×10^{12}
Iodine (^{129}I)	4.41×10^{-8}	1.21×10^{-10}	1.57×10^7	5.73×10^9
Chlorine (^{36}Cl)	2.3×10^{-6}	6.30×10^{-9}	3.01×10^5	1.10×10^8
Krypton (^{81}Kr)	3.03×10^{-6}	9.03×10^{-9}	2.29×10^5	8.36×10^7
Carbon (^{14}C)	1.21×10^{-4}	3.31×10^{-7}	5730	2.09×10^6

Radium (^{226}Ra)	4.33×10^{-4}	1.19×10^{-6}	1600	5.84×10^5
Argon (^{39}Ar)	2.58×10^{-3}	7.06×10^{-6}	269	9.83×10^4
Silicon (^{32}Si)	4.95×10^{-3}	1.36×10^{-5}	140	5.11×10^4
Strontium (^{90}Sr)	0.0241	6.65×10^{-5}	28.78	1.05×10^4
Hydrogen (^3H)	0.0558	1.53×10^{-4}	12.43	4540
Krypton (^{83}Kr)	0.0644	1.77×10^{-4}	10.756	3929
Radium (^{228}Ra)	0.121	3.31×10^{-4}	5.75	2100
Sulphur (^{35}S)	2.89	7.92×10^{-3}	0.240	87.51
Argon (^{37}Ar)	7.23	1.98×10^{-2}	0.0959	35.04
Radon (^{222}Rn)	66.0	0.181	0.0105	3.8235

Caesium 137 is a multiple radiation emitter with a gamma-beta energy of G: 32, 661.6 B: 511.6, 1173.2 KeV, sufficient to cause irradiation of various substances such as those present in seawater with a photon energy of 662 KeV.



Radioactive isotopes of cesium are a greater health concern than stable cesium. The most important exposure routes are external exposure to the radiation emitted by the radioisotope and ingestion of radioactive cesium-contaminated food sources.

Salts of Caesium is very soluble in water, as of 2005, caesium-137 is the principal source of radiation in the zone of alienation around the Chernobyl nuclear power plant. Together with caesium-134, iodine-131, and strontium-90, caesium-137 was among the isotopes with greatest health impact distributed by the reactor explosion.

Molecular damage results from the direct ionization of atoms that are encountered by beta and gamma radiation and by interactions of resulting free radicals with nearby atoms. Tissue damage results when the molecular damage is extensive and not sufficiently repaired in a timely manner.

Gastrointestinal absorption from food or water is the principal source of internally deposited cesium in the general population. Essentially all cesium that is ingested is absorbed into the bloodstream through the intestines. Cesium tends to concentrate in muscles because of their relatively large mass.

Biological effects of caesium ingestion in mammals

Adverse neurological, developmental, reproductive, genotoxic, and cancer effects have been observed in animal studies employing external exposure to sealed radioactive cesium sources, and are the result of the external gamma radiation, impaired motor activity, decreased thickness of cortical layers of the brain, and increased aggressive behavior were observed after the birth of rats that had been briefly exposed *in utero* to relatively high levels of external radiation from a ^{137}Cs source (Minamisawa et al. 1992; Norton and Kimler 1987, 1988).

In a advisory document by the Delaware Health and Social Services, USA, caesium 137 exposure pathway is described as a radioisotope and unstable chemical. Its radioactivity is measured by the number of atoms disintegrating per unit time. A Cs-137 atom emits radiation in the form of medium energy gamma rays, and to a lesser extent, high-energy beta particles, which disrupt molecules in cells and deposits energy in tissues, causing damage. Cs-137 is used in medical therapy for oncology, industrial radiography, radiation gauges, food irradiators and soil testing. It is also a potential plume component following a nuclear power plant incident. When a person inhales or ingests a radioisotope, it is distributed to different organs and stays there for days, months or years until it decays or is excreted.

Chlorine is a very reactive element that does not occur uncombined in nature. It is usually found bound with elements such as sodium, potassium, and magnesium.

The most common chlorine compound is sodium chloride (table salt), which is present in seawater, salt wells, and large salt deposits, often in association with other chlorides. Chlorine is produced commercially by the electrolysis of sodium chloride, and it can also be produced by oxidizing the hydrogen chloride in hydrochloric acid. Chlorine-36 is generated in the atmosphere by the spallation of argon-36 with cosmic ray protons, and in soil and rock by neutron activation of chlorine-35. Large amounts of chlorine-36 were produced by irradiating seawater during certain nuclear weapons tests conducted between 1952 and 1958.

Once taken in, chlorine-36 behaves in the body the same way as other chlorine isotopes. Chlorine is almost completely absorbed upon ingestion, moving quickly from the gastrointestinal tract into the bloodstream. The chlorine-36 that enters the bloodstream after ingestion or inhalation is quickly distributed to all organs and tissues of the body. Chlorine-36 is eliminated from the body with a biological half-life of 10 days.

While in the body, chlorine poses a hazard from the beta particles and gamma radiation. The main concern is the increased likelihood of cancer induction. It should also be noted that medical studies developed subsequent to the Chernobyl reactor accident is indicative of widespread spike in cancer in the general population arising from the consumption of contaminated milk and water.

Starting in 1991, a comprehensive monitoring of water and sediment contamination with radionuclides, as well as their washout from the Iput river catchment area was organized in order to test the prognostic performance of mathematical models that described the processes of radionuclide washout from catchment areas and their migration in bodies of water.

It should be noted that chlorine-36 on a Radiological Risk Coefficient indicates the following:

Lifetime Cancer Mortality Risk

Inhalation 9.6×10^{-11}
(pCi-l)

Ingestion 2.9×10^{-12}
(pCi-l)

Additional novel gamma irradiation potential can also be inferred from the following paper, "Removal of sodium and chlorine from seawater prior to neutron activation analysis for trace elements" by S. K. Nyarku and A. Chatt, JOURNAL OF RADIOANALYTICAL AND NUCLEAR CHEMISTRY, 1982.

According to a paper "Treatment of internal radionuclide contamination" by T. Jan Cervený, Ph.D. for the United States Army, the degree of intraluminal gastrointestinal exposure depends on transit time through the gut, which will vary widely from person to person.

The mean clearance times of the human digestive tract are stomach, 1 hour; small intestine, 4 hours; upper large intestine, 13-20 hours; and lower large intestine, 24 hours, resulting in a total mean emptying time of 42 hours. The much slower rate of movement in the large intestine places its luminal lining at higher risk for damage from nonabsorbable radionuclides.

Some relatively soluble radionuclides may not be absorbed due to acidic or caustic properties that fix them to tissue proteins.

One of the principal methods employed to remove undissolved solids from water, or other fluids, is to pass the fluid through a mechanical filter means, such as a filter screen, filter cloth, filter leaf or the like. With respect to the removal of dissolved impurities from water or other fluids, the use of ion exchange resins has become well known in the art.

In a typical process for removing dissolved impurities from water, commonly referred to as a demineralization process, the untreated water containing the dissolved impurities, such as salts or electrolytes, is passed through a bed of cation ion exchange resin.

As a result of the ion exchange between the cation ion exchange resin and the water, the salts are changed to corresponding acids. Thereafter, the water is passed through a bed of anion ion exchange resin wherein an ion exchange reaction removes the acids. As a result, there occurs a significant removal of dissolved impurities.

However, particular and unique problems are presented when the fluid contaminants are radioactive.

Similarly, the removal of dissolved solids by passage through a cation ion exchange bed of ion exchange resins also results in a build-up of radioactive materials within the cation ion exchange bed.

It is the present practice to permit concentration of radioactive materials to exist up to acceptable limits in a filter apparatus and thereafter to remove the radioactive filter structure as well as any radioactive demineralization resins for transport to a disposal tank.

A disadvantage attendant to the radiation concentration level limitation is that such radiation level occurs prior to the complete usage of the filter apparatus as well as the ion exchange materials.

More particularly, it is typically the case that the upper limit of radiation concentration in the cation ion exchange material occurs when the activity of the ion exchange material has been utilized to only a low fraction of its full ion exchange capability.

Known methods and apparatus for purifying such radioactive waste waters involve collection of the waters from around the facility through appropriate drainage into a sump.

Thereafter the sump water is pumped into a filtration and/or demineralization apparatus which removes the dissolved and undissolved impurities in order that the water so purified may be returned to the system for reuse or discharged appropriately outside the plant facility.

Such filtration and purification equipment is the type which requires removal of the active demineralization materials and the filter apparatus upon the occurrence of the upper limiting levels of radiation concentration.

Thus the known methods and apparatus are both costly by reason of their inefficient use of the purification means as well as limited in the amount of radio-active impurities which may be removed.

PRIOR ART PUBLICATION

1. Tokyo Electric Power Co. Fukushima Daiichi Nuclear Power Station, Nuclear and Industrial Safety Agency Report 26 March 2011, Mr Toshihiro Bannai, Director, International Affairs Office NISA/METI
2. How Radiation Threatens Health, Scientific American (Fukushima Daiichi Nuclear Power Station, seawater) March 15, 2011, Nina Bai.
3. CHANGES IN WATER-SALT EXCHANGE IN RADIOPHOSPHORUS-INDUCED RADIATION SICKNESS IN RABBITS, DIRECTORATE OF SCIENTIFIC INFORMATION SERVICES OTTAWA, Khvoinitskaya, M. A., Report Number AD0610886
4. WATER TRANSPORT AT CELL MEMBRANES, Canadian Journal of Biochemistry and Physiology, 1964 Jun; 42:945-53
5. Radiation and Human Health, Institute for Energy and Environmental Research, 6935 Laurel Avenue Suite 201 Takoma Park, MD 20912

6. Fluorescence in situ hybridization study on Chernobyl liquidators, Lawrence Livermore National Laboratory, Irene Jones (925) 423-3626 (jones20@llnl.gov) or Joe Lucas (925) 422-6283
7. Health effects in those with acute radiation sickness from the Chernobyl accident, Radiology and Nuclear Medicine Service, New Mexico Federal Regional Medical Center, 1501 San Pedro Boulevard SE, Albuquerque, NM 87108, USA, Mettler FA Jr, Gus'kova AK, Gusev I.
8. Pritchard, J, Herczeg, A, Lamontagne, S. 2000. The use of environmental tracers for estimating seasonal contributions of groundwater to stream flow. In CD Proceedings International Groundwater Conference "Balancing the Groundwater Budget", Darwin. International Association of Hydrogeologists
9. Ellins KK, Roman-Mas A, Lee R, 1990. Using ^{222}Rn to examine groundwater/surface discharge interaction in the Rio Grande De Manati, Puerto Rico. *Journal of Hydrology* 155:319-341
10. Cook, PG, Favreau, G, Dighton, JC, Tickell, S. 2003. Determining natural groundwater influx to a tropical river using radon, chlorofluorocarbons and ionic environmental tracers. *Journal of Hydrology* 277, 74-88.
11. Browne E, and Firestone, RB 1999. Table of isotopes, 8th Edition. Wiley and Sons, New York
12. Radioactivity in the Natural Environment. Lawrence Berkeley National Laboratory
13. Coale, K. H., and K. W. Bruland. "Oceanic Stratified Euphotic Zone as Elucidated by Th-234: U-238 Disequilibria," *Limnol. Oceanogr.* 32:189-200, 1985
14. ICS Industrial Chemical Solutions, Envirosorb Media.

Summary of the present invention

A seawater intake supply is measured by a analyzer device for one or more radionuclide dissolved or undissolved such as Cs-137 and device adapted to divert the flow of seawater from the intake supply to a trace radionuclide reactor stage to remove one or more radionuclide from seawater such that the seawater pre-treated is substantially free of one or more detected radionuclide prior to subsequent treatment of the pre-treated seawater into drinking or treated water of a desired quality and specification.

Description of the drawings

FIG 1 is a table depicting the various activity concentration of a selected range of radionuclide including Cs137 which has a half-life of about 30 years.

FIG 2 is a table showing the technical specification of the nuclear reactor utilized in the majority of BWR reactor design in current operation around the developed world. Fukushima nuclear power plant of Japan features an identical reactor to the table and further infers the potential ionic interaction between the fuel rod, cladding material, alloy steel structure and seawater.

FIG 3 illustrates the redundant coolant supply system identical to Fukushima nuclear power plant of Japan, the safety relief valves were believed to be compromised and potentially leaking fluid containing excessively high levels of radionuclide-laden material. Proximity to the coast infers potential contamination of the surrounding seawater, subsequent readings of seawater 10-20 kilometers from the nuclear power plant indicates high levels of Cs137 confirming the probability of the conjecture presented.

FIG 4 illustrates the coolant supply system identical to Fukushima nuclear power plant of Japan wherein point of failure of diesel generator A lead to the sequence of events where urgent injection of seawater was the only method to perform heat exchange of the reactor core, and spent fuel pools.

Interaction of seawater with MOX fuel rods in reactor no. 3 infers potential for downstream irradiation of various trace impurities present in seawater.

FIG 5 is a summarized data table indicative of the potential damage to mammalian cells from inhaled and or ingested radionuclide doses in the studies indicated at far right.

FIG 6 is a table illustrating the various naturally occurring radionuclides already present in seawater. Ionic interaction of Cs137 with the various trace radionuclide such as Pb have not been studied, while indirect irradiation of chlorides are inferred.

Various metal oxides from the steel alloy and fuel rod cladding with seawater under elevated temperature and prolonged irradiation with the reactor core, spent fuel pool are yet to be assessed for impact, however, correlations can be made with respect to Chernobyl 1986 nuclear reactor event.

In 2002, in a report "Radioactivity Monitoring of the Irish Marine Environment 2002" published by the Radiological Protection Institute of Ireland, results indicate higher than natural levels of radionuclide in seawater, seaweed and marine lifeforms such as fish stocks.

Cs137 levels not naturally occurring in seawater has been attributed to the Chernobyl 1986 nuclear reactor event.

FIG 7 is a table indicating the various half-life of radionuclide.

FIG 8 illustrates the decay mechanism of the radionuclide Cs137 and the respective energy levels during radioactive decay. Irradiation factor of Cs137 on trace impurities of seawater can thus be postulated with mathematical models that takes into account mean reaction space-velocity, mean temperature during irradiation and event probability of limited group interactions of material sets, including reactor core, fuel rod gross surface area and probabilistic rate of leakage of irradiation seawater into coastal seawater body, and probabilistic rate of leakage of irradiation seawater into coastal seawater body by way of marine vessel ballast pickup.

FIG 9 illustrates one preferred embodiment of the present invention.

FIG 10 is a table illustrating the known exposure window of Cs137 into the global environment

FIG 11 is a summarized table indicative of the possible pathway for cancer induction from ingestion of Cs137 or other forms of radionuclide beyond a set concentration activity. This indicates cancer induction probability for prenatal defects in mammals.

FIG 12 is an elaborated summarized table similar to that of table 11.

FIG 13 is an example distribution table wherein recordings of trace radionuclide in seawater identified as intake seawater for subsequent treatment into drinking water are supplied as input data. Multiple distribution tables can be further constructed for each trace radionuclide such as Cs137 in order to perform detection and diversion of the intake seawater for pre-treatment.

FIG 14 is an example of how the detection apparatus can be adapted to perform detection and subsequent diversion of intake seawater for pre-treatment in a seawater treatment plant for generating drinking water. The standard deviation for each distribution table and thus the corresponding trace radionuclide will differ depending on the allowed activity concentration level for the corresponding trace radionuclide.

FIG 15 shows a simplified equation model that is computer-implemented for modeling the contamination risk of seawater laden with one or more radionuclide transported from a plurality of marine vessels to within the loci proximity of a domain containing at least one seawater treatment plant.

FIG 16, FIG 17 shows high magnification of a zeolite granule surface structure (FIG 16) as compared to the high magnification diagram of a sand particle. Micro-crystalline structures present on the zeolite granule surface facilitates selective capture of one or more identified radionuclides from seawater to

yield substantially radionuclide-free pre-treated seawater for downstream conversion into drinking water in the seawater treatment plant.

FIG 18 shows a preferred embodiment of the present invention for use by a seawater treatment plant comprising a reverse osmosis bank further comprising a plurality of reverse osmosis (RO) filtration units.

FIG 19 shows a computer-implemented CFD (computer fluid dynamics) method to predict one or more variable output to estimate range of radionuclide contamination relative to a target seawater treatment plant within a control domain.

Preferred embodiment of the present invention

With reference to FIG 9, a seawater intake source 10 is identified and at least a portion of the seawater from source 10 is routed into analyzer module 20 for measurement and detection of trace radionuclide in the seawater.

A number of radionuclides such as cesium 137 (Cs137) are monitored by the analyzer module 20 storing a statistical distribution table such as a z-table in the electronic memory space in operative communication with the analyzer module 20.

A set point value indicative of a maximal activity concentration of the radionuclide associated with the z-table is computed to derive a standard deviation σ and the analyzer module 20 further adapted to trigger diversion of seawater from the intake source 10 into seawater circuit 20a if the measured signal from module 20 exceeds σ associated with the z-table of the linked radionuclide.

In one mode of the invention, the analyzer module 20 is adapted to store one or more z-tables (or other forms of statistical distribution table) each being associated with input data of a detected trace radionuclide. In one non-limiting example, and with reference to FIG 6 and FIG 7, several z-tables with their corresponding σ are stored in the memory space of the analyzer module 20.

In one non-limiting example of the present invention, the seawater flow from intake source 10 may be bypassed directly to the seawater treatment plant 30a during monitoring phase of the analyzer module 20 wherein none of the σ values of each z-table are exceeded.

If a determined σ value of a specified z-table of a radionuclide being monitored exceeds the indicative permissible activity concentration the analyzer module generates a control signal to a primer mover device such as a flow pump that diverts the flow of seawater from the intake source 10 into seawater flow circuit 20a leading into the selective radionuclide removal stage reactor 200.

Based on a normal probability density distribution routine, we can write the analyzer detection algorithm as follows:

```
t<-seq(-5.5,length.out=100)

max_x<-max(t)

d1<-dnorm(t,0,1)
d2<-dnorm(t,0,2)
d3<-dnorm(t,1,1)

max_y<-max(c(d1,d2,d3))

plot(t,d1,type='l',xlab="x",ylab="density",main="Normal Probability Densities")
lines(t,d2,lty=2)
lines(t,d3,lty=3)

leg.txt <- c("N(0,1)", "N(0,2)", "N(1,1)")
legend(max_x-2, max_y-0.005,c("N(0,1)", "N(0,2)", "N(1,1)"), col = c(3,4,6), text.col= "green4",lty =
c(1, 2, 3), merge = TRUE, bg='gray90')
```

```
dev.off()
```

With reference to FIG 6 and FIG 7, in another preferred embodiment of the present invention, we select 8 trace radionuclides for monitoring, detection and measurement by the analyzer device (module) 20:

```
N<-101
t<-seq(-2,2,length.out=N)
x<-t
xnorm<-rnorm(t,0,1)

par(mfrow=c(2,2))

a<-0.02
sigma<-0.85
y<-a*x+xnorm*sigma
r<-cor(x,y)
plot(-4:4, -4:4, xlab= 'x', ylab= 'y', main= "", sub = "", type = "n")
points(x,y,pch=19,cex=0.2)
legend(-3.9, 3.8,substr(paste("r=",r), 1, 8), bg='gray90')
```

```
a<-0.20
sigma<-0.7
y<-a*x+xnorm*sigma
r<-cor(x,y)
plot(-4:4, -4:4, xlab= 'x', ylab= 'y', main= "", sub = "", type = "n")
points(x,y,pch=19,cex=0.2)
legend(-3.9, 3.8,substr(paste("r=",r), 1, 7), bg='gray90')
```

```
a<-0.35
sigma<-0.5
y<-a*x+xnorm*sigma
r<-cor(x,y)
plot(-4:4, -4:4, xlab= 'x', ylab= 'y', main= "", sub = "", type = "n")
points(x,y,pch=19,cex=0.2)
legend(-3.9, 3.8,substr(paste("r=",r), 1, 7), bg='gray90')
```

```
a<-0.45
sigma<-0.2
y<-a*x+xnorm*sigma
r<-cor(x,y)
plot(-4:4, -4:4, xlab= 'x', ylab= 'y', main= "", sub = "", type = "n")
points(x,y,pch=19,cex=0.2)
legend(-3.9, 3.8,substr(paste("r=",r), 1, 7), bg='gray90')
```

```
a1<-0.30
sigma<-0.15
y<-a*x*x-xnorm*sigma
r<-cor(x,y)
plot(-4:4, -4:4, xlab= 'x', ylab= 'y', main= "", sub = "", type = "n")
points(x,y,pch=19,cex=0.2)
legend(-3.9, 3.8,substr(paste("r=",r), 1, 8), bg='gray90')
```

```

a1<-0.35
sigma<-0.2
y<-a*x*x*x+xnorm*sigma
r<-cor(x,y)
plot(-4:4, -4:4, xlab= 'x', ylab= 'y', main= "", sub = "",type = "n")
points(x,y,pch=19,cex=0.2)
legend(-3.9, 3.8,substr(paste("r=",r), 1, 7), bg='gray90')

```

```

a<--0.33
sigma<-0.3
y<-a*x+xnorm*sigma
r<-cor(x,y)
plot(-4:4, -4:4, xlab= 'x', ylab= 'y', main= "", sub = "",type = "n")
points(x,y,pch=19,cex=0.2)
legend(-3.9, 3.8,substr(paste("r=",r), 1, 7), bg='gray90')

```

```

a<--0.45
sigma<-0.00000
y<-a*x+xnorm*sigma
r<-cor(x,y)
plot(-4:4, -4:4, xlab= 'x', ylab= 'y', main= "", sub = "",type = "n")
points(x,y,pch=19,cex=0.2)
legend(-3.9, 3.8,substr(paste("r=",r), 1, 8), bg='gray90')

```

```
dev.off()
```

A simplified code in C can be implemented within the memory space of the analyzer module 20 as follows:

```

public static double Deviation(double[] Values, DeviationType CalculationType)
{
    double SumOfValuesSquared = 0;
    double SumOfValues = 0;
    //Calculate the sum of all the values
    foreach (double item in Values)
    {
        SumOfValues += item;
    }
    //Calculate the sum of all the values squared
    foreach (double item in Values)
    {
        SumOfValuesSquared += Math.Pow(item, 2);
    }
    if (CalculationType == DeviationType.Sample)
    {
        return Math.Sqrt((SumOfValuesSquared - Math.Pow(SumOfValues, 2) / Values.Length) /
(Values.Length - 1));
    }
    else
    {
        return Math.Sqrt((SumOfValuesSquared - Math.Pow(SumOfValues, 2) / Values.Length) /
Values.Length);
    }
}

```

```

    }
    public enum DeviationType
    {
        Population,
        Sample
    }

```

The stage reactor 200 is supplied electric power from a power supply circuit 200a and in one preferred embodiment of the present invention the stage reactor is a electro-coagulation radionuclide reactor stage, and in yet another embodiment of the present invention the stage reactor 200 is a ion-exchange reactor stage.

In some current seawater treatment plants such as seawater desalination systems featuring reverse osmosis (RO) units, if radionuclides are measured at the intermediate flow permeate it would indicate a high probability of contamination in the RO membrane or the ion-exchange beds within the untreated desalinated water flow, which is very costly to replace.

Stage reactor 200 can comprise of a electro-coagulate radionuclide removal stage with seawater placed within the reactor and anode-cathode bank with an applied DC current to cause selective coagulation of the radionuclide to the coagulate agent either disposed at the anode or cathode end. The coagulate agent may be a specified polymer or a metallic coat on either the anode or cathode thus allow efficient coagulate-radionuclide removal either in-situ at reactor stage 200 or downstream of reactor stage 200.

Pre-treated seawater substantially free of the trace radionuclide flows in circuit line 200b to a valve control junction 200c to be routed to flow circuit 20b that is operationally connected to seawater treatment plant 30a.

It should be noted that seawater treatment plant 30a can be a terrestrial-based facility such as a multi-stage flash distillation plant, a reverse osmosis desalination plant or some other variation such as multi-stage vapor compression plant etc., or a seawater treatment plant onboard a marine vessel such as a ship, a barge, offshore rig platform.

Mathematical modeling of ballast water discharge

In one preferred embodiment of the present invention, the novel radionuclide contamination route in seawater via transport of ballast water from marine vessels is modeled via a computer-implemented method by first identifying one or more discharge zone of a determined detection area.

With reference to FIG 19, a control domain boundary condition C10 is specified having a horizontal plane domain geometry of a specified height representing the volume of seawater body surrounding fixed computational mesh blocks of C50 and C60 with at least one identified seawater treatment plant TR10 and at least one intake boundary point specified at 200.

To reduce computational demand during modeling, the domain C10 may be specified as a multi-block configuration where the mesh block C20 and C30 are modeled based on the input variables related to the mean frequency of ballast discharged from a control population of marine vessels during a determined time interval. This can thus be defined within the computational domain as a discharge zone (C20 and C30).

The detection area would suitably encompass or within a determined loci proximity to one or more seawater treatment plant, and each discharge zone is utilized as a input variable domain set comprising the following input variables:

- 1) approximate frequency of marine vessels discharging ballast water within each discharge zone,
- 2) mean/median ballast discharge volume from the vessel population of the target discharge zone,
- 3) determined time interval of discharge for 1, 2,
- 4) contamination coefficient:

The contamination coefficient is derived from a risk score calculation by correlating the route hops or route points of each identified marine vessel against the radionuclide risk score of either all or at least one of the route hop/points where there is an elevated risk of pick-up of ballast water having higher than usual radionuclide contaminants.

Degree of resolution required of the contamination coefficient will determine the number of variables utilized in risk score calculation to derive the coefficient, and various tensor factors would have to be sufficiently incorporated to accommodate variability such as seasonal jetstream flows, reliability of data measured from each marine vessel, etc.

5) propagation probability based on identified turbulence transport equation model: because of the large number of variables some of which cannot be easily predicted with a fair degree of statistical confidence, the degree of mixing between the ballast water discharged from one or more identified discharge zone over a calculated time interval (which should be longer than the time scale interval of step (3), is extrapolated by a given turbulence transport model (which in the simplest form can be a Reynolds averaged Navier Stokes [RANS] turbulence model) based on localized number of discharge spots within the identified discharge zone.

Since tidal influences can be fairly consistent and can be forecasted ahead, we would develop the turbulence model chosen (such as RANS) based on a maximal number of discharge points wherein such maximal value is the mean frequency of vessels discharging ballast water within the time interval of step (5) multiplied by a peak factor, notably to account for variations in cargo traffic volume depending on the time period, for example.

Based on a “globalized” domain boundary within the identified discharge zone, the time-series calculated stabilized radionuclide activity concentration can be forecasted – to which its accuracy would depend on two factors; choice of turbulence model relative to the localized condition of the discharge zone and deviation in variable inputs which can be subsequently corrected.

With reference to FIG 19, the turbulence flow depicted at TU10, TU20, TU30 and TU40 would have to be identified and modeled as either dependent variables (tidal effects) based on a smaller error coefficient, or dependent variables (climatic-influenced wave-tidal flow) based on a large error coefficient – the mixed zone depicted at boundary C40 would be one of the last input variables where the mean radionuclide contaminant range is calculated as a fluid volume source for seawater intake point 200 of seawater treatment plant TR10.

Multivariate analysis using the above variable inputs (and the selected choice of turbulence transport model to derive some of the inputs) provides at least one output variable such as the activity concentration of seawater that is collected by the seawater treatment plant identified either within or in proximity to the identified discharge zone (or zones).

In one such example, a multifactor analysis can be computer-implemented to determine the selected output variable for modeling and operational monitoring and tracking, with reference to FIG 15, an example non-linear factor analysis equation model is utilized for computation in a computer-implemented system wherein 1000 shows the simplified model where $Z_{sub.i}$ is the observable variables, f being the latent factors for each individual and ϵ being the measurement error.

The functional relationship between non-linear coefficients such as variables at step (2) and step (4) are corrected by means of the additional nonlinear terms as indicated in the simplified variable equation model 2000.

This solution thus allows for consistent modeling of the possible radionuclide contamination effects brought over to the identified discharge zone by marine vessel ballast water transport. Using the various other embodiments of the present invention, the entrapment and gradual accumulation of dissolved radionuclides downstream of an identified seawater treatment plant is significantly mitigated at an attractive cost/effectiveness ratio.

Plant Design Variation A

In one variation, the stage reactor 200 is a ion-exchange reactor stage that is designed specifically for removal of radionuclides such as Cs-137 to provide sufficient isolation of the contaminated seawater from the subsequent downstream seawater treatment equipment stages of the treatment plant 30a.

Plant Design Variation B

In this plant variation the intake source of FIG 9 is a sampling intake source of a drinking water supply system routed to the analyzer module 20 for monitoring and detection of one or more radionuclide to which the drinking water supply is diverted into flow circuit line 20a and into pre-treatment reactor stage 200 to remove the detected trace radionuclide from the drinking water supply system, and further re-mineralized to a desired drinking water specification prior to routing to flow circuit 20b into a treated drinking water accumulation pool at 30a.

Plant Design Variation C

In this variation and embodiment of the present invention, a granulated zeolite stage comprising one or more granulated zeolite bed plant captures a range of radionuclide material present in intake seawater of a seawater treatment plant to yield a substantially radionuclide free intake pre-treated seawater prior to conversion of the intake pre-treated seawater into drinking water.

For a multi-stage zeolite bed plant, measurement of partially treated seawater yielded from a first zeolite bed stage is measured for trace radionuclide material prior to passing the partially treated seawater to a second zeolite bed stage, wherein the measured partially treated seawater inter-stage between the first and second zeolite bed stages will represent deterioration in performance of the first zeolite bed stage if the measured partially treated seawater exceeds a determined threshold range.

Variant CD-1, Reverse Osmosis Filtration Inter-stage System

With reference to FIG 18, another embodiment of the present invention is hereby disclosed wherein a first filtration bank FB1 is supplied with seawater source SW1 to yield a first permeate that is flowing in first permeate line SWPL2.

The filtration bank FB1 comprises a plurality of filtration membrane devices such as ultrafiltration apparatus/units to remove suspended particles, selected contaminants etc, to yield first permeate which in normal operating routine is flowing from SWPL2 into the second filtration bank FB2 comprising a plurality of reverse osmosis (RO) units to yield a second permeate flowing in second permeate line SWP2 which is of a determined water specification.

The first permeate line SWPL2 is adapted with a detection point SWP1 to perform monitoring and detection of a determined number of radionuclide matter that is present in first permeate generated from first filtration bank FB1.

During the instance where first permeate flowing from first filtration bank FB1 has a detected concentration activity count that is indicative of a above maximum radionuclide contaminant level (RCL), the first permeate is diverted from line SWPL2 to a selective radionuclide treatment stage depicted at 200 wherein radionuclide matter detected is suitably removed to form a first permeate substantially free of the radionuclide to within a determined "safe" RCL range.

The "treated" first permeate yielded from reactor 200 is fed back into SWPL2 from "treated" first permeate line SWPL3 for subsequent filtration by second filtration bank FB2 into the second permeate product flowing in line SWP2.

Zeolite manufacture and preparation

Zeolites are microporous inorganic crystalline materials with uniform pore dimensions. The zeolite framework consists of TO₄ tetrahedra units, where T is predominantly either a Si⁴⁺ or Al³⁺ atom located at the center of the tetrahedron. Other T-atoms such as (Fe, Ti, Ge, Ga, and Se) can be incorporated usually in small amounts, or as impurities, and for special purposes.

Tetrahedra units are joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. Since the microstructure is determined by the crystal lattice it is precisely uniform with no distribution of pore size. This pore size regularity makes zeolites different from other molecular sieves such as the microporous charcoal and amorphous carbon.

The crystalline zeolite framework carries a negative charge, and its magnitude depends on the amount of isomorphically substituted Al^{3+} .

This charge is balanced by cations localized in non-framework positions (incavities or channels) to obtain a neutral net charge of the structure. Typical cations include the alkaline (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the alkaline earth (Mg^{2+} , Ca^{2+} , Ba^{2+}) cations, as well as NH_4^+ , H_3O^+ , TMA^+ (tetramethylammonium) and other nitrogen- containing organic cations.

The framework charge and cations are important as they determine the ion exchange properties of zeolites. Zeolites with low Al^{3+} content or constituted exclusively of Si^{4+} in the tetrahedral sites have low negative or neutral framework charge and therefore exhibit a high degree of hydrophobicity and poor ion exchange capacity

A powder can be formed to be granular zeolite, in an appropriate size for further using or packaging and shipping. Therefore, the granular zeolites should have good strength after firing. The binders are added to improve their strength. Several of the popular kinds of binder used are kaolin and talcum. In this research, the kaolin and talcum are used as binders.

Rocks that are rich in kaolinite are known as china clay or kaolin. Kaolinite is a clay mineral with the chemical formula. $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.

The chemical composition of kaolin consisted of the following oxides expressed as percentage by weight; Al_2O_3 , 39.8 %; SiO_2 , 46.3 %; H_2O , 13.9 %.

It is a single layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedra.

Talcum is a clay mineral with the chemical formula $Mg_3(Si_2O_5)_2(OH)_2$. The chemical composition of talcum consisted of the following oxides expressed as percentage by weight; SiO_2 , 57.76%; MgO , 31.35 %; other, 10.89 %.

It is a double layer silicate minerals based on the valency of the counter balancing cations. In marked contrast with minerals of the kaolin, extensive elemental substitution within the double layer lattice is the rule rather than the exception [4]. Sizes of clay affect the strength and the shrinkage percentage on firing (of clay when it dries or when it is fired). The finer grind of clay has stronger and higher percentage of shrinkage on firing.

While the various preferred embodiments have been disclosed and described, it will be understood that there they are not to limit the invention by such disclosure, and are intended to cover all modifications, alternative methods and steps within the spirit and scope of the invention as defined in the following claims:

CLAIMS:

1. A method for pre-treatment of dissolved and undissolved radioactive matter (radionuclide) in seawater prior to reclamation of seawater into drinking water in a seawater treatment plant, comprising the steps:

identifying a seawater intake source and collecting seawater from seawater intake source;
measuring collected seawater for trace of one or more radionuclide;
diverting collected seawater for electro-coagulation of one or more radionuclide to one or more elected coagulant agent to yield coagulant-laden seawater;
removing the elected coagulant and one or more radionuclide from coagulant-laden seawater to obtain pre-treated seawater substantially free of one or more radionuclide;
routing the pre-treated seawater to seawater treatment plant for reclamation into drinking water,

wherein collected seawater is diverted for electro-coagulation if one or more radionuclide trace level in collected seawater measured exceeds a determined trace standard deviation value associated with one or more radionuclide.

2. The method of claim 1 wherein electro-coagulation comprises passing an electric direct current (DC) through collected seawater disposed between an anode apparatus and a cathode apparatus to cause radionuclide containing dissolved ions, suspended solids to coagulate with elected coagulant agent.
3. The method of claim 1 wherein collected seawater is measured for trace radionuclide comprising one or more trace radionuclide analytical measurement signal.
4. The method of claim 3 wherein one or more trace radionuclide analytical measurement signal is digitally supplied to an analytical processor to generate one or more trace radionuclide statistical distribution table and one or more corresponding determined trace standard deviation value of each said trace radionuclide statistical distribution table.
5. A system for pre-treatment of dissolved and undissolved radioactive matter (radionuclide) in seawater prior to reclamation of seawater into drinking water in a seawater treatment plant, comprising the steps:

a seawater intake apparatus for identifying a seawater intake source and seawater intake apparatus collecting seawater from seawater intake source;

an analyzer device for measuring collected seawater for trace of one or more radionuclide and analyzer device deriving a first trace radionuclide measurement signal;

a first fluid pump for diverting collected seawater for filtration in a suspension filter, of one or more suspended radionuclide particle and suspension filter for removing the suspended radionuclide particle to yield first pre-treated seawater volume substantially free of one or more suspended radionuclide particle based on one or more first computed trace deviation signal;

analyzer device for measuring first pre-treated seawater volume for trace of one or more dissolved radionuclide and analyzer device deriving a second trace radionuclide measurement signal;

a second fluid pump for diverting first pre-treated seawater volume for electro-coagulation in an electro-coagulation module, of one or more dissolved radionuclide to one or more elected coagulant agent to yield coagulant-laden seawater and electro-coagulation module removing the elected coagulant and one or more dissolved radionuclide from coagulant-laden seawater volume to obtain second pre-treated seawater volume substantially free of one or more dissolved radionuclide based on one or more second computed trace deviation signal;

a third fluid pump for routing second pre-treated seawater volume to seawater treatment plant for reclamation into drinking water,

wherein first computed trace deviation signal is generated by analyzer device and first computed trace deviation signal is indicative of at least one first trace radionuclide measurement signal exceeding a reference set point first trace radionuclide activity concentration value stored in the analyzer device.

6. The system of claim 5 wherein second computed trace deviation signal is generated by analyzer device and second computed trace deviation signal is indicative of at least one second trace radionuclide measurement signal exceeding a reference set point second trace radionuclide activity concentration value stored in the analyzer device.
7. The system of claim 5 wherein analyzer device comprising at least one electronic processor.
8. A method for pre-treatment of dissolved radioactive matter (radionuclide) in seawater prior to reclamation of seawater into drinking water in a seawater treatment plant, comprising the steps:

identifying a seawater intake source and collecting seawater from seawater intake source;
measuring collected seawater for trace of one or more dissolved radionuclide;

diverting collected seawater for selective radionuclide removal of one or more dissolved radionuclide to yield pre-treated seawater substantially free of one or more dissolved radionuclide;
routing the pre-treated seawater to seawater treatment plant for reclamation into drinking water,

wherein collected seawater is diverted for selective radionuclide removal if one or more dissolved radionuclide trace level in collected seawater measured exceeds a determined trace standard deviation value associated with one or more dissolved radionuclide.
9. The method of claim 8 wherein each determined trace standard deviation value is indicative of a determined activity concentration associated with a corresponding dissolved radionuclide.
10. The method of claim 8 wherein collected seawater is measured for trace radionuclide comprising one or more dissolved trace radionuclide analytical measurement signal.
11. The method of claim 10 wherein one or more dissolved trace radionuclide analytical measurement signal is digitally supplied to an analytical processor to generate one or more dissolved trace radionuclide statistical distribution table and one or more corresponding determined trace standard deviation value of each said dissolved trace radionuclide statistical distribution table.
12. The method of claim 8 wherein selective radionuclide removal comprises one or more electro-coagulation process stage wherein each electro-coagulation process stage further comprising a power supply circuit passing an electric direct current (DC) through collected seawater disposed between an anode apparatus and a cathode apparatus to cause radionuclide containing dissolved ions, and colloids to coagulate with one or more elected coagulant agent.
13. The method of claim 8 wherein selective radionuclide removal comprises one or more ion exchange process stage.