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PROCESS OF DECONTAMINATING MATERIAL CONTAMINATED WITH RADIOACTIVITY

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This invention relates to a method of decontaminating objects contaminated with radioactive materials. More particularly, the invention relates to a method of decontaminating equipment which has been employed in the processing of radioactive materials and includes a method which involves the use of special solvents.

In various industrial processes involving treatment or handling of radioactive substances, it is necessary after comparatively short periods of time to treat the various pieces of equipment employed to decontaminate such equipment from radioactivity. For example, in many processes involving the chemical separation of the numerous constituents of a radioactive mixture, such pieces of equipment as precipitators, filters, centrifuges, catch tanks and the like become contaminated with radioactive substances to such an extent that exposure of personnel to the equipment is hazardous.

As illustrative of a process utilizing equipment which, after comparatively short periods of time, becomes contaminated, mention may be made of a process for the chemical separation of the constituents found in a neutron irradiated uranium mass.

Naturally occurring uranium contains a major portion of $_{92}U^{238}$, a minor portion of $_{92}U^{235}$ and small amounts of other substances such as UX_1 and UX_2. When a mass of such uranium is subjected to neutron irradiation, particularly with neutrons of resonance or thermal energies, $_{92}U^{238}$ by capture of a neutron becomes $_{92}U^{239}$ which has a half life of about twenty-three minutes and by beta decay becomes 93^{239}. The 93^{239} has a half life of about 2.3 days and by beta decay becomes 94^{239}. Thus, neutron irradiated uranium contains both 93^{239} and 94^{239}, but by storing irradiated uranium for a suitable period of time, the 93^{239} is converted almost entirely to 94^{239}.

In addition to the above mentioned reaction, the reaction of neutrons with fissionable nuclei such as the nucleus of $_{92}U^{235}$ results in the production of a large number of radioactive fission products. For example, when an atom of $_{92}U^{235}$ undergoes fission, two fragments are formed. These fragments vary sufficiently in their masses and hence their atomic numbers to give some 34 elements, all of which initiate further reaction chains with the emission of radiations. These chains are the source of all of the radioactivity that renders isolation of any one of the products of irradiation of uranium so difficult. The radiations include: (1) beta or high speed negative electrons with variable energy contents, and therefore, different velocities, (2) soft gamma, or electromagnetic radiation similar to X-rays but with a shorter wave length and moderately higher energy content, (3) hard gamma similar to the soft type except that it has a shorter wave length and higher energy content, and (4) neutrons.

In general, the stability of an atom depends on the ratio of protons to neutrons in the nucleus and certain ratios, therefore, result in an excess energy content that must be emitted as radiation before a stable end product is formed. While most naturally occurring isotopes are stable and therefore not radioactive, those resulting from fission have proton-neutron ratios such as to cause internal instability. As a result, they tend to stabilize and in the process emit their excess energies in one of five general ways.

In the first place, an atom may emit a beta particle from the nucleus where the only possible source of a negative electron is from a neutron which gives both a positive and negative charge. The loss of the negative charge converts the neutron to a proton and there is a gain of one in atomic number and hence a transmutation to the next higher element. Such a change, of course, alters the proton to neutron ratio and may result in a stable atom, although this is not necessarily true.

In the second place, a beta particle of lower energy content may be emitted, thus forming the next higher element while still leaving the nucleus with too great an energy content to be stable. The first beta particle may then be followed by another one to form the second higher element in the atomic series which again may or may not be stable.

Thirdly, a beta particle of intermediate energy may be emitted to form an unstable isotope of the next higher element which, due to its excess energy, may give off a gamma ray rather than a beta particle. This process also may result in either a stable or an unstable atom.

Fourthly, the beta-decay of a fission product may leave the nucleus in a state of excitation higher than the binding energy of a neutron in that nucleus. The neutron is then immediately emitted, and the rate of decay of the neutron-emitting activity observed is just that of the preceding beta activity.

Finally, an unstable atom may emit a gamma ray which strikes an electron in one of the inner shells of electrons and ejects it in such a condition that it has some of the properties of the nuclear beta particle. Since the electron, which in this case is known as a photoelectron, does not originate in the nucleus, there is no change in the atomic number and the process, like that involved in the emission of a gamma ray, is known as internal conversion.

With the exception of elements 43 and 61, the fission products formed by the above discussed reaction are all well known elements with normal chemical properties, the only point of difference between them and the corresponding natural elements being that they are composed of unstable isotopes. As brought out above, due to their internal instability they either undergo transmutation to other elements or stabilize themselves internally by the emission of one or more of the previously-mentioned radiations. Consequently, stabilization may involve no change in atomic number or a change of several units. The average length of the fission chains, that is the number of transmutations, is about 3.2 but some may be as long as 6. In general, a decay chain has emitted a total of 25 to 30 m. e. v. as radiation by the time it is complete.

The fission of $_{92}U^{235}$ yields two general types of elements, namely heavy and light. The light fission products possess atomic numbers between 30 and 46 and include radioactive zinc, gallium, germanium, arsenic, selenium, bromine, krypton, rubidium, strontium, yttrium, zirconium, columbium, molybdenum, 43, ruthenium, rhodium, and palladium.

The heavy fission products resulting from neutron irradiation of $_{92}U^{235}$ possess atomic numbers ranging from 47 to 63 and include radioactive silver, cadmium, indium, tin, antimony, tellurium, iodine, xenon, cesium, barium, lanthanum, cerium, praseodymium, neodymium, 61, samarium and europium.

Thus, the neutron irradiated uranium mass comprises plutonium together with fission products, the latter being extremely radioactive. Generally speaking, the neutron irradiated uranium mass, advantageously in the form of slugs, is removed from the irradiation zone and allowed

to age for varying periods, advantageously a period of about 60 days. At the end of this aging period, the mass is subjected to chemical treatment for isolation of the plutonium and, if desired, for separation of certain groups of individual fission products.

At the present time, there are several commercially feasible processes for obtaining plutonium from such a neutron irradiated mass among which are the "bismuth phosphate" process and the "wet fluoride" process. These processes are more fully described in copending application Ser. No. 519,714, filed January 26, 1944, by Thompson and Seaborg, now U. S. Patent 2,785,951. In each of these processes, it is generally the practice to dissolve the slugs after they have been subjected to the aging period and by appropriate chemical manipulation involving precipitation, filtration and/or centrifugation and the like to recover a solution of plutonium or in some cases to recover a solution of the desired radioactive fission products or both.

In both of these processes, numerous items of equipment such as centrifuges, precipitators, tanks, piping, and the like are exposed to highly radioactive solutions and thus become contaminated after comparatively short periods of use. Since the equipment, generally speaking, is constructed of stainless steel, brass and other materials of similar nature, any method employed to decontaminate this equipment must be of such a nature as to substantially avoid corrosion or destruction of the equipment.

In addition, it is generally the practice to operate laboratories in connection with industrial processes for treatment and separation of radioactive materials such as the type described above. In these laboratories, the equipment also becomes contaminated with highly radioactive materials and hence must either be destroyed or subjected to decontamination operations. As is usually the case, the bulk of the equipment in such laboratories is made of glass and hence no decontamination process can be employed which has destructive effects upon such glass equipment.

Numerous attempts have been made to devise a process of decontaminating both industrial and laboratory equipment which has been exposed for considerable period of time to radioactive materials. It has been found that radioactivity may be removed from such contaminated equipment by numerous acids. However, the use of such acids is undesirable in that they exhibit a highly corrosive action upon the metal surfaces of industrial equipment of the type described above. Attempts were made to overcome this activity by reducing the concentration of the acids employed, but it was found that although substantial portions of radioactivity were removed, sufficient radioactive contamination remained upon the equipment to make exposure thereto still hazardous.

For instance, it was found that nitric acid will remove some contamination from contaminated equipment without undue corrosion. However, decontamination by means of nitric acid alone was found to be incomplete and a dangerous concentration of radioactivity still remained upon surfaces so treated. It was then found that the residual activity could be removed by a nitric acid-hydrogen fluoride acid decontamination. However, the hydrogen fluoride acid corroded both the metal equipment and glass to such an extent that the use of such a decontaminating solution could not be recommended.

We have found that radioactive contamination may be removed from objects contaminated therewith by treatment with an alkali metal hydroxide solution which advantageously contains certain additives such as hydroxy-carboxylic acids and salts thereof without the attendant disadvantage of corrosion of equipment under treatment.

It is accordingly an object of this invention to provide a process for decontaminating objects contaminated with radioactive materials.

It is further object of this invention to provide a process for removing radioactive substances from equipment contaminated therewith by the use of special solvents which have no corrosive action upon the equipment under treatment.

Still another object of this invention is the provision of a method of decontaminating equipment which has been exposed to radioactive substances by means of treatment with an alkali metal hydroxide solution.

Still another object of this invention is to provide a process of removing contaminating radioactivity from equipment which comprises contacting said equipment with an alkali metal hydroxide solution containing a compound selected from the group consisting of hydroxy-carboxylic acids and salts thereof.

It is still another object of this invention to provide a process of decontaminating equipment which involves removing a portion of said contamination by means of nitric acid and thereafter removing the remaining contamination by means of a solution containing sodium hydroxide and a tartrate and/or citrate.

Still another object of this invention is the provision of a solution for removing radioactive substances from materials contaminated therewith containing an alkali metal hydroixde and a citrate and/or tartrate.

These and other objects of our invention will become apparent to those skilled in the art upon becoming familiar with the following description.

In accordance with our invention, the equipment to be decontaminated is, generally speaking, first treated with a reagent for removing at least a portion of the radioactivity present. Although any material non-corrosive under the conditions obtaining may be employed for this purpose, we have found that non-corrosive acids such as nitric acid are particularly advantageous. Such a procedure is recommended whenever a substantial quantity of radioactivity is present as the contaminating substance. However, in certain instances the initial partial decontamination may be dispensed with and the equipment contacted directly with our new decontaminating liquid.

While the conditions to be observed in the initial step of that modification of our process involving a preliminary removal of radioactivity may be widely varied, generally speaking, advantageous results may be obtained when the concentration of the preliminary solvent is maintained at such a point as to substantially eliminate corrosion of the equipment under treatment. The point at which the concentration should be maintained may vary depending, among other things, upon the particular equipment under treatment, the solution utilized for preliminary purification, the concentration of radioactivity to be removed and the like. For instance, when utilizing nitric acid as the preliminary solvent in decontaminating metals which have been exposed to the radioactivity present in a solution of fission products, it has been found that advantageous results may be obtained by employing nitric acid in concentrations of up to 65% and preferably from 35% to 60%.

The temperature to be employed at the preliminary removal step of our process also is subject to variation, depending, among other things, upon the particular solvent utilized, the equipment under treatment and the concentration of radioactivity to be removed. Generally speaking, we have found that when utilizing a non-corrosive acid such as nitric acid, temperatures of between room temperature and the boiling point of the treating liquid give advantageous results in our preliminary step. We have obtained excellent decontamination of stainless steel equipment at temperatures of about 65° C.

The time of contact between the equipment under treatment and solvent also varies depending upon the solvent, the concentration of solvent, and the degree of contamination. Another factor which must be considered in connection with the time of contact is the temperature at which the preliminary treatment is conducted.

For instance, if a comparatively high temperature is employed, a shorter time of contact is utilized and a longer time would be advantageously employed if a comparatively low temperature is maintained during the initial purification. When utilizing nitric acid in a concentration of 35% to 60% and at a temperature of 65° C. or higher, excellent decontamination has been obtained by exposure of the equipment to the nitric acid for a period of one to two hours. Of course, if desired, a shorter or longer period of exposure may be employed, but due regard must be given to possibility of corrosion of the equipment due to over-exposure on the one hand while at the same time considering the possibility of failure to substantially remove radioactivity contamination due to under exposure on the other hand.

Following the preliminary removal of radioactive contamination, the equipment is then subjected to treatment with an alkali metal hydroxide such as sodium hydroxide. Although sodium hydroxide is preferred because of its availability and comparatively low cost, other alkali metal hydroxides such as potassium hydroxide, lithium hydroxide, rubidium hydroxide and cesium hydroxide may be utilized if desired.

The concentration of the hydroxide solution employed in the practice of our invention is advantageously maintained comparatively low. For example, concentrations of alkali metal hydroxide up to 20% have yielded particularly advantageous results. Excellent results have been obtained when utilizing a hydroxide concentration of 5% to 20% inclusive. Generally speaking, if a preliminary acid treatment is employed, it is desirable to utilize a solution containing some excess alkali in order to prevent acidification of the solution by any residual acid from the initial purification step which may remain in contact with the material to be decontaminated.

The decontamination which may be effected by the alkali metal hydroxide solution is greatly increased when certain additive agents are incorporated therein. Particularly advantageous agents which may be employed in connection with the alkali metal hydroxide solutions are the hydroxy-carboxylic acids and water soluble salts of such acids. Examples of such materials are tartaric acid, sodium tartrate, potassium tartrate, citric acid, sodium citrate, potassium citrate, lactic acid, sodium lactate, potassium lactate, malic acid, sodium malate, potassium malate, glycollic acid, sodium glycollate, potassium glycollate and the like.

We have obtained particularly advantageous results in the practice of our invention when employing as additive agents such compounds as the polyhydroxy polycarboxylic acids and water soluble salts thereof, for example tartaric acid, sodium tartrate, citric acid, sodium citrate and the like. The concentration of such additive agents in the decontaminating solutions are advantageously maintained below 20%. Concentrations of 1¼% to 20% additive have been found to be particularly effective in increasing the decontamination obtained in the practice of our invention.

Generally speaking, the temperature utilized in the alkali treatment step is subject to variation and advantageous results have been obtained at temperatures from about room temperature to the boiling point of the decontaminating liquid. Generally speaking, temperature of approximately 65° C. gives particularly advantageous results.

The time of contact between the equipment under treatment and our decontaminating solution may vary depending upon the particular solution involved, the degree of contamination and the particular type of equipment under treatment. Generally speaking, the equipment is maintained in contact with the decontaminating liquid for a period of time of about one hour. If a preliminary treatment is employed, the final decontamination step may be advantageously carried out in a shorter period of time than the preliminary step.

In addition to the additives mentioned above, in certain instances when dealing with certain types of contamination which have different properties depending on whether or not they are in the oxidized or reduced state, it may be desirable to include in the decontaminating liquid a reagent which converts the contamination into a soluble form under the conditions obtaining. For example, in the decontamination of equipment which has been exposed to liquids containing ceric phosphate, it is particularly advantageous to include in the original acid wash, if utilized, a reducing agent to reduce the ceric phosphate to acid-soluble cerous phosphate. While any reducing agent may generally be employed, we have obtained very advantageous results by utilizing hydrogen peroxide to accomplish this reduction. Generally speaking, 1 to 2% of hydrogen peroxide is suffiicent to bring about the desired reduction of ceric phosphate to its acid soluble cerous phosphate form. When utilizing hydrogen peroxide, in order to prevent the decomposition of the peroxide before it reaches the contaminated vessel, it is advantageously added directly to each vessel under treatment as 30% hydrogen peroxide solution just before the vessel is brought into contact with the nitric acid solution.

The processes of our invention may be more readily understood by reference to the following specific examples:

Example I

A 1" x 1" x 1/16" stainless steel panel was hung in a semi-works extraction catch tank for a period of one week during a process run on the chemical separation of a neutron irradiated uranium metal slug. The panel was then removed and a count was taken to determine the radioactive contamination present. The count of this sample was found to be 132.5 divisions per minute in beta activity as measured by a radiation measuring electroscope; the gamma activity of this panel was so high that it could not be measured with the available Geiger-Muller counter which was capable of measuring up to 5000 counts per minute. The sample was then subjected to treatment with a 60% nitric acid solution at 65° C. for approximately ½ hour. Following this treatment the sample was subjected to treatment with a solution containing 20% sodium hydroxide and 20% sodium tartrate. The sample thus treated was exposed to the same radiation measuring devices and found to have a beta count of 0.12 division per minute and a gamma count of 416 counts per minute.

Example II

A stainless steel panel having the same dimensions as that of Example I and having been exposed for one week in a catch tank containing a solution of neutron irradiated uranium metal was contacted with a 60% nitric acid solution and thereafter contacted with a solution containing 10% sodium hydroxide and 1¼% sodium tartate Prior to this treatment the beta activity of the sample was 86.7 divisions per minute on the electroscope and the gamma activity of the sample was too high for measurement on the Geiger-Muller counter. After treatment in accordance with this example, beta activity was 0.07 division per minute, and the gamma count was 14 counts per minute.

Examplet III

A stainless steel panel such as that utilized in Example I and having been subjected to the same degree of contamination as that in Example I, was found to have a beta count of 75.3 divisions per minute and a gamma count too high for measurement. This sample was treated with 60% nitric acid at 65° C. for a period of ½ hour and thereafter treated with a solution containing 5% sodium hydroxide and 1¼ sodium tartarate at 65° C. for a period of ½ hour. The sample was then counted and the beta activity was found to be 0.06 division per minute, and

the gamma activity was found to be 20 counts per minute.

Example IV

A stainless steel panel subjected to contaminating conditions in a semi-works catch tank was counted and found to have a beta activity of more than 5000 counts per minute. This panel is then soaked for a period of ½ hour at 65° C. in 65% nitric acid. Following this treatment it was soaked in a solution containing 20% sodium hydroxide and 10% sodium citrate at 65° C. for a period of ½ hour. The beta activity was determined and found to be 541 counts per minute.

It is to be understood, of course, that the above examples are given for purposes of illustration and hence may be widely departed from without departing from the spirit of our invention. For instance, if desired, the various steps of acid treatment and alkali treatment may be repeated, hence increasing the decontamination obtained by our process. However, a single cycle may be all that is necessary to reduce the contaminating radioactivity to a point below human tolerance therefor.

In some instances, a repetition of either the preliminary purification step, if utilized, as well as repetition of the second purification step may be desirable to accomplish substantially complete decontamination. For instance, in some cases, it has been found that treatment of a contaminated object with our new decontaminating liquid for a period of one hour gives substantially the same decontamination as is obtained when the contaminated object is maintained in contact with the same decontaminating liquid for a period of two hours. However, if the contaminated object is maintained in contact with the decontaminating liquid for a period of one hour and thereafter contacted with a fresh supply of decontaminating liquid of the same composition as that originally employed, increased decontamination is obtained.

If desired, the decontaminating liquid utilized in removing radioactivity may be formed in situ or may be prepared prior to its addition to the treating vessel. In decontaminating large pieces of equipment such as a catch tank, the decontaminating liquid may be advantageously fed into the vessel undergoing treatment and maintained therein under the desired conditions. In treating smaller pieces of equipment, it is advantageous to maintain the treating liquid in a separate vessel and immerse the article to be decontaminated therein for a suitable period of time.

Other methods which may be employed in decontaminating objects in accordance with our invention involve spraying the object with out new decontaminating liquid. Our process is also adaptable to batch and continuous operation. For example, continuous decontamination may be effected by passing the contaminated objects through a spray of decontaminating liquid. Contaminated objects may also be suspended from a suitable traveling belt which may be designed to pass through a bath containing our decontaminating liquid. In those modifications of our invention wherein in the contaminated object is immersed in a bath of decontaminating liquid, it may desirable to provide the bath with a suitable agitating device, such as a series of paddles, to insure circulation of decontaminating liquid about all parts of the contaminated object.

While our invention has been described with reference to certain modifications and certain specific examples, it is not intended that the invention should be limited by such description. Therefore, changes, omissions, and/or modifications may be made without departing from the spirit of our invention as defined in the appended claims which are intended to be limited only as required by the prior art.

We claim:

1. A process of decontaminating an object contaminated by contact with an aqueous solution containing ions of uranium fission products which comprises contacting said object with an acid to remove at least a portion of the contamination and a water soluble salt of a hydroxy carboxylic acid.

2. A process of decontaminating a metallic object which has been contaminated by contact with an aqueous solution containing ions of uranium fission products which comprises contacting said object with a non-corrosive acid to remove at least a portion of the contamination and thereafter substantially completely removing the remaining contamination by contacting the partially decontaminated object with a solution containing an alkali metal hydroxide and a water soluble salt of a polyhydroxy polycarboxylic acid.

3. A process of decontaminating a metallic object which has been contaminated by contact with an aqueous solution containing ions of uranium fission products which comprises contacting said object with a non-corrosive acid to remove at least a portion of the contamination and thereafter substantially completely removing the remaining contamination by contacting the partially decontaminated object with a solution containing an alkali metal hydroxide and a water soluble citrate.

4. A process of decontaminating a metallic object which has been contaminated by contact with an aqueous solution containing ions of uranium fission products which comprises contacting said object with nitric acid, thereby removing at least a portion of the contamination, and thereafter contacting the resulting partially decontaminated object with an aqueous solution containing sodium hydroxide and sodium tartrate.

5. A process of decontaminating a metallic object which has been contaminated by contact with an aqueous solution containing ions of uranium fission products which comprises contacting said contaminated object with nitric acid in a concentration of 35% to 60% to remove at least a portion of the contamination, thereafter contacting the partially decontaminated object with a solution containing up to 20% to an alkali metal hydroxide and up to 20% of sodium tartrate.

6. A method of decontaminating material which has been exposed to a solution of fission products resulting from the neutron irradiation of uranium, said solution including ceric phosphate, which comprises contacting said material with an acid solution containing a reducing agent to remove at least a portion of the contamination therefrom, and thereafter contacting the resulting partially decontaminated material with a solution containing an alkali metal hydroxide and a compound selected from the group consisting of hydroxy carboxylic acids and salts thereof.

7. A process of decontaminating industrial equipment which has been contaminated by contact with an aqueous solution containing ions of uranium fission products which comprises immersing said equipment in a bath containing up to 65% nitric acid at a temperature of about 65° C. for a period of from two to three hours, and thereafter immersing said equipment in a second bath containing a solution comprised of up to 20% sodium hydroxide and up to 20% sodium tartrate, and removing said equipment from said second bath.

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