Usages of Nanomaterials in the Treatment of Primary Coolant Water for Pressurized Water Reactors

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The application of nano silica extracted from kaolinite, bentonite and rice straw is proposed as treatment material for the purification of primary coolant water of pressurized water reactors. Three elements were used to simulate some radionuclides that can be released in the primary coolant water namely, strontium, nickel and cobalt. Various batch experiments were performed including selection of efficient sorption nanomaterial, optimum operational weight ratio (element/nano material), selectivity of the nano silica for elements used, determination of the equilibrium curve of sorption process, and desorption behavior of nanomaterial with pH and temperature variation. The samples were analyzed using the inductively coupled plasma emission spectrometer. Silica of kaolinite, bentonite and rice straw showed the same results in the efficiency/capability removing the three elements used. Silica form of rice straw has been selected as nano-treated materials for economic and environmental reasons. The sorption process reached equilibrium after 30 min approximately. The experiments demonstrated that the sorption reaction of elements by the nano-silica is an irreversible reaction with the change of temperature and pH. The obtained results indicated that using the nano silica increased the safety margin of the treatment stage in the multi barrier concept.

Keywords: Radionuclides; Nano-silica; Sorption; Primary coolant water treatment; Safety barriers

Introduction
Nanotechnology is the macromolecular research and technology. In other words, the length scale shall be between 1-100 nanometer. When modifying the material on a nanoscale, it can display different useful and extraordinary properties that have not been observed [1]. Many research papers have been focused on the preperation, characterization and application of nanomaterials in industry [2-4]. Nanoparticles obtained by applying nanotechnology shows high efficiency in many areas such as nuclear power plants. Copper nanoparticles are utilized in several applications related to the safety and stability of equipment in nuclear power plants [5], but these particles must be stored far from the ignition sources [6]. V.F. Petrunin has experimentally shown, adding 5 to 10% of the U³⁺O²⁻ nanocrystalline powder to a traditional coarse powder for reduction of temperature or the increasing of fuel volume [7]. Also, the Massachusetts Institute of Technology (MIT) has applied alumina nanoparticles that cover fuel rods to avoid the accumulation of any bubbles on hot elements. As a stable element of a high melting temperature, alumina which is an addition of aluminum and oxygen, is stable and has a high melting temperature. There are also potential

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safety applications because nanomaterials are capable of transporting large quantities of heat rapidly from the coolant stored in Emergency Core Cooling Systems (ECCS) [8]. In addition, studies have replaced activated carbon by carbon nanotubes (CNTs), in chemical preignition, to increase sorption selectivity and removal efficiency. On the other hand, CNTs and titanite nanofiber show good performance in eliminating the radioactive elements from water [9]. The disadvantages of multi wall carbon nanotubes (MWCNTs) are that they accumulate in the body in a very complex structure and cannot be easily twisted [10]. The disadvantages of these nanomaterials that have appeared during the fabrication methods include complex processing parameters, low yield, low efficiency, long duration, and costly equipment and processes [11]. Considering the pressurized water reactor (PWR), the primary coolant water is continuously purified from fission products (FP), activation products (AP) and corrosion products (CP) through the chemical volume control system (CVCS) using four ion exchange vessels [12]. This method depends on ion exchange vessels which have many defects. These defects include high cost, low selectivity media that can remove target ion in the presence of other ions and it should provide an acceptable product quality for safe final disposal. In addition, the resin does not offer suitable stable product forms, minimize waste volumes, and maximize waste loadings in stabilized matrices [13]. Therefore, studies try to find an alternative which has the same role and does not cause problems such as those that occur in solidification and disposal processes.

The aim of this work is to select a suitable inorganic nanomaterial for the purification of primary cooling water taking into consideration, cost, availability and safety aspects

**Experimental Work**

*Materials used:*

**Nano-materials**

Kaolinite, Kaolin clay or white clay is rich in kaolinite mineral and is also classified as layered silicate mineral. Kaolinite molecules can easily convert to other form of molecules due to a heat-absorbing process or heat-hydroxyl removal process [14-16]. Bentonite, which is alumino silicate mineral, has the structure of one alumina octahedral layer sandwiched between two silica tetrahedral layers [17]. Nanoparticles, known as silica nanoparticles or nano silica, are the basis for many researches because of their stability, low toxicity and their ability to work with a group of molecules and polymers [18-20]. After the conversion of materials into nanoparticles, the organic materials became inorganic materials. These nanomaterials were prepared in Mina University by different methods: sol gel method and ultrasonic method, but for preparation of Nano-silica from rice straw ash, chemical precipitation method was used [21].

**Characterization of nano materials:** nano materials were analyzed using different devices as follows:

**X-ray diffraction (XRD):**

It is performed by shooting a known wave length with definite energy of x-ray on the fine powder sample. The x-rays diffraction is designed in the form of peaks, which are compared with the standard data base. The shape of the peak indicated the degree of material crystallinity. The area under peak determines the amount of this material. In addition, XRD results can reflect the phase analysis of the material (single or second phase due to the presence of impurities or deformation) [18]. The model of apparatus used, in the present work, is XRD 6000, Shimadzue Wavelength 0.15406 nm, Voltage 40kV, Current 30 mA.

The average particle size can be determined by The Scherrer’s equation [19]:

$$D_p = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta}$$

Where $D_p$ is the size of the particle, $\lambda$ is the wavelength of X-ray, $\beta_{1/2}$ is the wavelength of full width half maximum and $\theta$ is the peak position.

**The energy dispersive x-ray spectroscopy (EDX):**

This analysis was performed on the samples to determine qualitative elemental analysis [20]. This analysis depends on the interaction between x-ray projected on the sample and the electrons of different energies exist around the nucleus of the atom in the sample. The apparatus model used is OXFORD attached to scanning electron microscope JEOL-JSM-5400.
Transmission electron microscopy (TEM):
An electron beam with short wave length is projecting on a dispersive sample in ethanol. The interaction between electrons and the specimen produce an image with very high accuracy and magnification [21]. This analysis was made to examine the morphology and particle size of the three nano materials. The model of apparatus used is TEM Model-JEOL-100 CX.

Simulation of radioactive elements
The radioactive fission products (FP), activation products (AP) and corrosion products (CP) are replaced by strontium (Sr), nickel (Ni) and cobalt (Co) chemical elements, respectively. Fission products are the yield of uranium fission reaction; these products can dissolve and migrate from cracks of nuclear fuel to water coolant such as 90Sr which is β-emitter with half-life of 28.8 years. Activation Products are chemical elements activated by the neutron flux such as 63Ni which emits beta particles with a half-life of 96 years. Corrosion Products come from the corrosion of the structure materials in contact with the primary coolant such as 60Co of half-life 5.2714 years [22-24]. For the simplicity during discussion; the nano silica from Kaolinite is defined as silica 1, nano silica from Bentonite is silica 2 and nano silica from rice straw is silica 3.

Preparation of the element stocks
Each element stock solution (Sr, Ni, Co) was separately prepared as follows:
a - 1 gram of each element (strontium chloride hexahydrate (SrCl2·6H2O), nickel chloride hexahydrate (NiCl2·6H2O) and cobalt chloride hexahydrate (CoCl2·6H2O) was dissolved in 1000 ml of distilled water.
b - A mixture of these elements was prepared using 50 mL of each stock solution.

Methods
The constant conditions that were considered during the experiments are as follows:
- Room temperature equals 22 ±2 0C
- pH of distilled water is 6
-Samples were shaken with a shaker model (SK-600, Lab Companion) for 1 hr at 120 r.p.m
-Samples were put in a centrifuge model (Heraeus Labofuge 200) for 10 min at 5000 r.p.m for precipitating the suspended particles.
- Final solutions were analyzed by inductively coupled plasma emission spectrometer (ICP) model (720 ICP-OES, Agilent Technologies).

Selection of efficient nano material
The experiment was prepared by adding 0.05 gm of nano material to the chemical elements. The amounts of Sr, Ni and Co were 0.3 gm, 0.5 gm and 0.4 gm respectively. The salts were dissolved in 100 ml of distilled water. The samples were taken through two days

Maximum weight ratio
- The mixture of Sr, Ni and Co elements with concentrations 329, 247 and 248 mg/l respectively was prepared with 1gm of silica 3.
- The mixture of Sr, Ni and Co elements with concentrations (100 to 400 mg/l) was prepared with 0.01gm of silica 3.
Weight ratio calculation: element weight (mg/l)/silica weight (mg/l)

Selectivity
The primary water reactor may contain many types of radionuclides. Therefore, the experiment 2.B.1 was repeated using the mixture of the three elements. The samples were taken through two days.

Equilibrium experiment
(a) Low concentrations and low time range:
- the sample was prepared using 0.01 gm of Silica 3 and 400 mg/l of elements during two hours.
(b) High concentrations and longtime range:
- the sample was taken from the first experiment and analyzed after three months.
For conservative conditions, the experiment was repeated using 0.05 gm of silica 3 and the sample was taken after 3 months to test the stability of reaction equilibrium.

Desorption experiments
During the operation of a nuclear power reactor, the addition of boric acid and lithium hydroxide to the coolant is necessary to control pH. Meanwhile, by the action of different phenomena such as radiolysis effect by temperature and radiation, the proper value of coolant pH becomes difficult to specify [25].
On the other hand, according to Le Chatelier principle; when increasing the temperature of water, the equilibrium will move to decrease the
temperature; consequently, the forward reaction will be favored [26]. Therefore, the impact of the pH value and temperature on the desorption process of silica 3 was tested. The following experiments were prepared by mixing:

**In case of pH experiment**
- 1 gm of nano silica was added to 50 ml of each element stock.
- 1 Molar of NaOH and 1 M of HCl solutions were used for varying the pH values from 2 to 9.
- The beakers were shaken for one week at 120 r.p.m.

**In case of temperature experiment**
- 1 gm of nano silica was dissolved in 50 ml of each element stock solution.
- The beaker was shaken at 25 0C for one day.
- Many samples were taken each 2 hr along 1 day.
- The previous steps were repeated at about 40 0C and 60 0C

**Results and Discussion**
The material prepared from Kaolinite, Bentonite and Rice straw ash by ultra-sonic and sol gel and chemical precipitation methods were analyzed using different devices as follows.

Figure (1) illustrates the results of XRD analysis. The strongest three peaks in a) are at 2θ 32, 19, 49 with intensity values 157, 75 and 76. The strongest three peaks in b) are at 2θ 27, 21 and 60 with intensity values 217, 46 and 44. The strongest three peaks in c) are at 2θ 25, 12 and 38 with intensity values 64, 47 and 36. Fig. (1.a), the peaks at different 2θ values predicted the formation of nano materials. In Fig. (1.b) and c), the peaks formed are not completely different from the XRD patterns of the raw materials. The disparities of nano materials patterns in three cases occurred due to different preparation methods. Sharp peaks in the providence of the crystallinity of the nanomaterial are formed. The particle size is calculated. The average of particle size is 32.2 nm, 37.4 nm and 19.9 nm for nano materials from RSA, B and K, respectively.

Although the three nano materials were prepared in different ways, they gave the same adsorption capacity. This is evidence that they contain the same element in the original structure. This element, which is responsible for the process of adsorption, became clearer after converting them only nano materials.

Figure (2) shows the results of EDX analysis. In case of the three nano materials, the EDX analysis indicates lower percentage of oxygen relatively to the percentages of silicon, which prove the presence of silicon not silica. In case of nanoparticles from RSA; the percentages were 47.9% silicon (Si) and 2.4% oxygen. In case of nanoparticles from B; percentage of Si was 63.3% and oxygen 2%. In case of nano particles from K; percentages of Si is 51.8% and oxygen is 7.6%. The silicon shows the dominant particle in the three nano materials. Because silicon is tetrahedral valency which exists in contact with lower percentages of oxygen, the silicon phase has the tendency to capture other elements to reach a stable form. This is a major cause of adsorption process, which reveals the reliability and stability of the process that is further evidenced by the following results.

On the other hand, percentages of S, Fe and Al are the second higher percentages in nano material from RSA, B and K, respectively. These values cannot be ignored in these nanostructures which can attribute to the stabilization of adsorption process and need more separate investigations.

By the application of TEM instrument, the images of the nano material from RSA appear well scuttle particles on carbon grade and in spherical shape as shown in Fig. (3.a). In Fig. (3.b), nano particles from B have been agglomerated in two pictures but with good dispersion in the third picture. The particles shape is completely different in this case, may be as a needle or sphere. In Fig. (3.c), the images of nano material from K appear to be in two states. The first reflects agglomerated spherical particles and the second exhibits good scattering form. The average particle sizes are 17.2 nm, 12.5 nm and 25 nm for nano material from RSA, B and K, respectively.

The determination of particle size from XRD and TEM shows the following ranges; (17- 33 nm), (12-38 nm) and (20-25 nm) for nano material from RSA, bentonite and kaolinite, respectively. The material prepared from Kaolinite, Bentonite and Rice straw by ultra-sonic and sol gel and chemical precipitation methods, produces inorganic nanomaterial in the form of silica [21]. For simplicity silica from kaolinite, bentonite and rice straw is noted as silica 1, silica 2 and silica 3, respectively.
USAGES OF NANOMATERIALS IN THE TREATMENT ....

Fig. (1): XRD of the three nano materials (a) RSA, (b) B, and (c) K
Fig. (2): EDX pattern of three nano materials from (a) RSA, (b) B, and (c) K.
USAGES OF NANOMATERIALS IN THE TREATMENT UNIT

Figure (4) illustrates the effect of the variation of time with the removal percentages of the different elements with the three nano materials to investigate their sorption capacity. Silica 1, 2 and 3 show approximately the same capacity of sorption for the three elements; 88 to 90% for Sr, 74 to 77% for Ni and Co during the two days. The Figure shows that Sr has the highest value of sorption. The high removal percentage of Sr may be due to its higher atomic radius compared with Ni and Co [27-29]. The higher radius has the higher tendency to fixation.

The aim of this assay is selecting a suitable nanomaterial that can be applied in the treatment unit (CVCS). However, by comparing the three materials, Kaolinite and bentonite are useful elements in nature. On the other hand, rice straw is considered an agriculture waste. The incineration of rice straw causes a serious environmental problem. In addition, extraction of silica in nano shape from rice straw ash is a useful transformation of waste to form a cheap by-product material of different applications. Accordingly, silica 3 was chosen to be under study to be an alternative option of the organic resin in treatment unit.

Figure (5) illustrates the influence of weight ratio of element to the silica 3 on the removal percentage of the element. In addition, Table (1) lists the different weight ratios (element/Si 3) with their removal percentage. This Table provides further clarification of the data in Fig. (5). The Figure is designed to calculate the best weight ratio that can be applicable during the operation of the unit. In case of Sr element, the best ratio of 97.4% was reached by the addition of 1g Silica 3 and 329ppm Sr (high weight of silica and low concentration of element). In case of Ni and Co, no obvious difference could be detected during the variation of weight ratio. The removal percentage changed from 60 percent to 70 percent.

During the normal/accident operational conditions, many radionuclides may be dissolved in the coolant water. Therefore, the treatment unit shall have the capability to efficiently remove the radionuclides. A competition can be built between radionuclide to be sorbed by silica 3 once the three elements are in a mixed solution. Figure (6) demonstrates the effect of competition behavior of elements on the sorption capacity of silica 3; the results shown in this Figure are unexpected. In spite of the same concentration conditions, there is no change in sorption capacity in the two cases separately or in mixture.

During the operation of treatment unit, the equilibrium of sorption capacity is considered an important factor in the design of the unit to quantify the contact time and the rate of contaminated flow with silica 3. Figures 7 (a and b) shows a the change of removal percentages or sorption capacity with time. Two ranges of concentration and time have been studied to define the equilibrium of sorption reaction. Figure (4a) reveals the change of the equilibrium curve of elements mixture during 5 min to 120 min with 0.01 gm of Silica 3. The concentration of Sr, Ni, Co is 400 ppm each. Fig. (4b), for conservative conditions, the time range was from 1 hr to 2160 hr with 0.05 gm of Silica 3. The equilibrium was reached after 30 minutes in both cases (a, and b).

According to the inter-effect of all steps in the management of radioactive waste, the proposed treatment using nano silica shall study its stability during conditioning and its efficiency in the multi barrier concept during disposal [30-31]. Therefore, the desorption experiments (variation of pH and temperature) are important to evaluate the fixation durability of the elements on Silica 3 under different conditions.

Different pH values were applied as an indicator of chemical reaction. Therefore, it was essential to study normal variation of pH values during the sorption process of mixed solutions as shown in Fig. (8). The pH raised with a small value (from 6 to 7) until the equilibrium of sorption reaction was reached (30 minutes). This may be due to the formation of Sr hydroxide. From 30 minutes to 3 hours, no change in the pH values appeared. Constant pH value indicated that there was no chemical reaction. No chemical reaction indicates no desorption process.

Figure (9) demonstrates the removal percentage of the three elements by Silica 3 in solution of different of pH values. The removal percentage of the three elements increased as pH value increased as shown in the Fig.9 (a, b, and c). However,
the higher removal percentage of Ni and Co can be due to the precipitation of elements at high pH values. Meanwhile, these results can give confidence of safety during burial of these elements. By the effect of cement matrix (of containers and solidified agent), pH of the disposal media can raise to 14.

During the normal conditions, the temperature of coolant water, in PWR, is high and also, the temperature in the disposal site can be increased due to radiation released from radionuclides. Figure (10) shows the temperature change with the removal percentages of elements by Silica 3. The three elements showed the same behavior; no change occurred in their removal percentage during the different values of temperature from 25 to 60°C.

From different researches, the use of organic resins in ion exchanger for removing Sr, Ni and Co was not efficient. The most prominent species used were the charcoals, phenolic resins, polysaccharides or keratin as protein. Various disadvantages have appeared through the application of these materials. Some examples were: their capacity was very small, they were very sensitive for swelling, they did not possess any stability during thermal path or radiological path. In other cases, they could remove Sr for 80% but for other elements the removal is about 30% only [34-36].

In this work, the applied inorganic nano materials succeeded in the purification of the elements from primary coolant water in a satisfied range of removal percentages. Despite their tiny diameters and very small sizes, they were very effective materials with high capacity. The use of nano silica increased the stability.

Fig. 6: Sorption affinity of silica 3 in a mixture of the three elements

(a) Low concentrations and low time range (b) High concentrations and long time range (conservative range)

Fig. 7: Equilibrium curve of sorption reaction of silica 3 with the three elements.

Fig. 8 pH of the solution during the sorption process
Fig. 9: Effect of pH variation on the sorption capacity (a) effect of pH variation with Sr, (b) with Ni and (c) with Co. Despite the three elements were in mixture during the experiments, the results of each element are shown separately to accurately track the behavior of each element.

Fig. 10: Effect of temperature on the removal% of elements by silica 3 (a) Sr, (b) Ni and (c) Co.
Conclusions
The present study aims at making use of the advantages of nanotechnology, to find a suitable nanomaterial for the treatment process of the primary coolant water of pressurized water reactors (PWR). In addition, some operational conditions were determined using the results of the present experiments. The material selected reduces different problems resulting from using organic resin. Various results have been obtained from these preliminary experiments as follows:

- Nano silica extracted from Kaolinite, Bentonite and rice straw ash shows the same results for the removal of the three elements used in the experiment. Silica from rice straw ash (Silica 3) has been selected as a nano-treated material for economic and environmental reasons.

- Each element has its own sorption capacity with Silica 3, therefore each radionuclide/element shall be studied separately or in a mixture.

- Affinity of Silica 3 for Sr is higher than those for Ni and Co.

- In the case of these three elements Sr, Ni, and Co, there is no change in the sorption capacity of the two cases separately or in the mixing of elements.

- The removal behavior of other elements shall be detected or tested.

- The fixation of elements on Silica 3 seemed to be permanent without any reversible reaction.

- The equilibrium of sorption reaction occurred in 30 min.

- Further investigations shall be performed to analyze the sorption behavior in case of the mixture of the three elements; no competition was found among the three materials with silica 3.

- The optimum conditions of sorption process are at weight ratios of Sr, Ni and Co to Silica 3, 0.05, 0.037 and 0.037 respectively.

- The sorption capacity of elements on the Silica 3 increases from low to high pH value and demonstrates highest percentages in alkaline medium.

- The sorption capacity of elements on the Silica 3 shows irreversible reaction with the variation of temperature.

Finally, from these preliminary experiments, Silica 3 can be concluded as a good nano material for the treatment and removal of elements from the primary coolant water. In addition, it will effectively contribute to the concept of multiple barriers for the disposal site.

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