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TECHNICAL NOTE

Sorption properties of stainless steel membranes impregnated with titanium dioxide sorbent

Aleksander Bilewicz

Abstract High-temperature sorption of corrosion products from primary cooling circuit is an effective method for radiation reduction in pressurize and boiling reactor plants. We have developed a suitable high temperature resistant adsorbent by impregnating a porous stainless steel membrane with titanium oxide. The adsorption studies of corrosion products in soluble and insoluble forms indicate that the stainless steel membrane impregnated with TiO_2 combines high affinity of TiO_2 for transition metal cations with a high mechanical stability of the porous steel membrane under high-temperature and high-pressure conditions.

Key words high temperature adsorption • titanium oxide • impregnated membrane

Introduction

During operation of pressurized and boiling water reactors small amounts of corrosion products are released into the coolant. These corrosion products are activated in reactor core and transported around the plant. When the activated corrosion products deposit, they may cause serious radiation problems [9]. The primary contributor to radiation level is ^{60}Co because of its long half-life and high gamma-ray energies. Therefore, the removal of ^{60}Co, as well as non-radioactive cobalt, is necessary to reduce radiation level. Different strategies have been developed to minimize radioactivity generation, transport and deposition in the cooling systems. One of these consists of the permanent and thorough cleaning of the cooling water from ions and particles [5]. For removing of ions, inorganic ion exchangers like ZrO_2aq. and TiO_2aq. are very efficient materials for sorption of radionuclides from aqueous solutions [3, 4]. They are high-temperature and radiation resistant and can be used for removal of radioactive corrosion products from the primary circuit of PWR and BWR [7]. One of the disadvantages of these materials is the irregular shape of the grains and poor mechanical stability, especially under high-temperature and high-pressure conditions [1]. For increasing mechanical resistant, the inorganic ion exchangers were calcined, incorporated in an alumina carrier [4, 6], polymer matrix [8], porous titanium sponge [6] and porous stainless steel membrane [2]. Titanium oxide, calcined at 600°C, exhibited a high compressive strength, but its specific surface area was very small which resulted in a low cobalt capacity (0.01 meq g^{-1}) [6]. TiO_2-Al_2O_3 adsorbent possessed a larger capacity (0.08 meq g^{-1}), but the compressive strength decreased in hydrothermal conditions due to pyrohydrolysis of Al_2O_3 [6].

A. Bilewicz
Department of Radiochemistry,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland,
Tel.: +48 22/ 811 27 35, Fax: +48 22/ 811 1532,
e-mail: abilewic@orange.ichtj.waw.pl

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The present work describes experimental results of our studies on high-temperature sorption of some radioactive corrosion and fission products on porous stainless steel membranes impregnated with TiO_2 sorbent.

Experimental

Preparation of membranes

The TiO_2 sorbent was precipitated inside a porous metal matrix. The porous stainless steel discs (diameter = 13 mm, thickness = 3 mm) were used as support. The membranes were formed as follows:

- air from the membrane was removed under vacuum,
- the membrane was immersed in tetraisopropyl orthotitanate for 20 hours,
- the membrane was shaken with 1 mol dm^{-3} LiOH solution for 5 hours, washed with deionized water and dried at 50°C to attain constant mass. The procedure was repeated 5–7 times.

Solutions

The sorption properties of the impregnated membranes were studied in a solution simulating boiling water reactor (BWR) coolant. The following radionuclides: ^{58}Co, ^{54}Mn, ^{65}Zn, ^{51}Cr, ^{125}Sb, ^{110m}Ag, and ^{85}Sr (supplied from Amersham International, England) were used as radiotracers. Before sorption experiments, the solutions were equilibrated with an autoclave material for 300 h at 280°C. After equilibration, the speciation of radioactive solution (amounts of ions and particles) was measured in the following procedure: the water from the autoclave after cooling was pumped through an acetate filter (pore size 0.45 μm). The filter and filtrated solutions were measured by γ-ray spectrometry. To estimate the amounts of particles below 0.45 μm and ions, the solutions after filtration were shaken with a strong acidic resin (Dowex 50 × 8) for 24 h. Next, the solution was separated from the resin and measured again.

Equipment

High-temperature sorption experiments were carried out in high-pressure equipment (Fig. 1). Feed water from the tank was pumped into the autoclave and heated to 280°C, then passed though the impregnated stainless steel membrane. The membrane was heated inside the autoclave. Feed water before sorption process and effluent from the column were analyzed by γ-ray spectrometry.

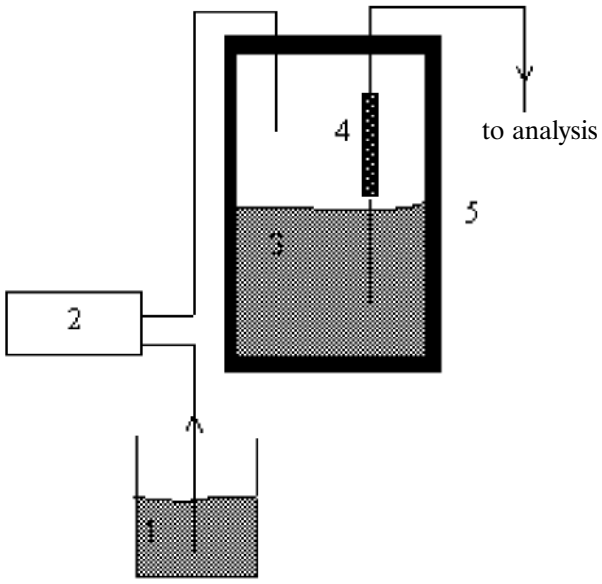

Fig. 1. A scheme of the high-temperature sorption equipment. 1 – tank of radioactive solution; 2 – HPLC pump; 3 – high-temperature (280°C) radioactive solution; 4 – HPLC stainless steel column; 5 – autoclave.

From the ratio of activity of the feed solution (A_i) and activity of the solution after passing throughout the membrane (A_f) decontamination factors (D_F) were calculated.

Results and disscusion

The stainless steel membranes impregnated with TiO_2 were studied at high-temperature and high-pressure conditions in long term dynamic experiments. Table 1 shows the decontamination factor values for membranes impregnated with TiO_2 after passing through 1.5, 6 and 10 dm^3 of radioactive solution. As shown in Table 1, the efficiency of purification of radioactive solution at high-temperature from most hazardous activated corrosion products was very high. The decontamination factor values for ^{58}Co, ^{65}Zn and ^{54}Mn,

Table 1. High-temperature of radioactive solution on sorbent membranes.

Membrane	D_F						
	^{58}Co	^{65}Zn	^{54}Mn	^{51}Cr	^{125}Sb	^{85}Sr	^{110m}Ag
Membrane without sorbent (t = 280°C)	2	2	–	23	>600	3	11
Membrane impregrated with TiO_2 after passing 1.5 dm^3 of solution (t = 280°C)	550	>600	600	50	>600	900	>1000
Membrane impregrated with TiO_2 after passing 6 dm^3 of solution (t = 280°C)	>600	>600	>600	70	>600	4	1
Membrane impregrated with TiO_2 after passing 10 dm^3 of solution (t = 280°C)	>600	>600	>600	65	>600	2	1
Membrane impregrated with TiO_2 after passing 1.5 dm^3 of solution (t = 25°C)	7	5	–	5	–	5	2

Table 2. Speciation of radionuclides in autoclave solution.

Radionuclide	Per cent of radioactivity		
	Particles >0.45 μm	Particles <0.45 μm	Ions
^{58}Co	45	0.9	54
^{65}Zn	45	1.3	53
^{51}Cr	46	26	28
^{85}Sr	8.8	0.5	91
^{125}Sb	18	82	0
^{110m}Ag	45	3.5	51

Table 3. Decontamination values for particles >0.45 μm, particles <0.45 μm and ions on stainless steel membrane impregnated with TiO_2 at 280°C at flow 90 $cm^3\ h^{-1}$ after passing 4 dm^3 of radioactive solution.

Radionuclide	D_F		
	Particles >0.45 μm	Particles <0.45 μm	Ions
^{58}Co	70	1	>300
^{65}Zn	80	2	>300
^{54}Mn	60	3	>300
^{51}Cr	–	4	3
^{110m}Ag	50	1	1
^{125}Sb	90	>500	–
^{85}Sr	–	3	4

at the beginning of the experiment were between 500–600, and after passing 6 dm^3 of radioactive solution through the membrane increased to more than 600 (activity in the effluent was under limit of detection) and did not change during the experiment. D_F for Sr^{2+} and Ag^+ rapidly decreased after passing 3 dm^3 of radioactive solution. At room temperature, the D_F for all radionuclides studied were much lower and varied from 2 to 7.

Since the feed water in the autoclave contains radionuclides in both ionic and solid forms the decontamination factor for particles up to 0.45 μm, below 0.45 μm and ions were studied. Tables 2 and 3 present speciation of radionuclides in the feed water and the decontamination factor values for solid and ionic species on membrane impregnated with TiO_2.

The results indicate that the membrane is effective as ionic and mechanical filter. Filtration of the solution was efficient and more than 98% of particles >0.45 μm remained on the membranes.

For divalent transition metal ions, the decontamination factors were very high, but sorption efficiency of transition univalent (Ag^+) and trivalent (Cr^{3+}) metal cations was relatively small. As mentioned previously, on the basis of the thermodynamic data, at 280°C the high efficiency of divalent transition metal sorption is related to the formation of spinel type compounds like cobalt, manganese or zinc metatitanate [1, 6]. Divalent strontium as a not d-electron metal ion is unable to form spinel with TiO_2.

The results presented in this paper show that the stainless steel membranes impregnated with TiO_2 combine high affinity of TiO_2 for transition metal cations with high mechanical stability of the porous steel membrane under high temperature and pressure conditions. The membranes impregnated with TiO_2 are promising materials for decontamination of cooling water from activated corrosion products in nuclear power plants.

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