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Review of Liang Zhao thesis

„Magnetic sorbent for the removal of cesium from aqueous solutions"

Supervisor: Prof. Andrzej G. Chmielewski

1. Introduction

The two types of water-cooled reactors are pressurized water reactors (PWR) and boiling water reactors (BWR). Both use so called light, i.e. normal, water, but with slightly differing cooling mechanisms. In a BWR, the water turns into steam in the reactor core and is then pumped directly to the turbines that power electrical generators. In a PWR, the primary loop of coolant flowing through the core is at very high pressure so it will remain a liquid. In BWR reactors situated on ocean coast as coolant is used ocean water. Such cooling system is in Fukushima Power Plants.

On 11 March 2011, a massive earthquake of magnitude 9 on the Richter scale hits the eastern coast of Japan. It led to loss of all onsite power sources resulting in serious accidents at the three operating Fukushima Daiichi reactors, which were classified as level 7 on the International Nuclear and Radiological Event Scale (INES).

The Fukushima I Nuclear Power Plant consists of six General Electric BWR with a power of 4.7 GW. Between 21 March and mid-July 2011, around $2.7 \cdot 10^{16}$ Bq of cesium-137 entered the ocean. However, the Fukushima coast has some of the world's strongest currents and these transported the contaminated waters far into the Pacific Ocean, thus causing great dispersion of the radioactive elements. Fukushima's radioactive ocean water arrives even at West Coast of Canada and two radioactive cesium isotopes, i.e. cesium-134 and cesium-137, have been detected offshore of Vancouver.

For this reason Mr Liang Zhao decided to search for new sorbents of radioactive cesium isotopes from aqueous media. To easy remove these isotopes Author decided to use ferromagnetic adsorbent. The dissertation research of Mr Liang Zhao was carried out under the supervision of Professor Andrzej G. Chmielewski, who has significant scientific achievements in this field of chemistry.

2. Characteristics and opinion about thesis

Chapter 1 of thesis (1 page) contain the objective of dissertation.

Chapter 2 contain literature review (20 pages). But there is too much about nuclear energy problems (11 pages) in comparison with problems of sorption for radioactive isotopes, including Cs-134 and Cs-137 (10 pages). Chapter 2 should also contain description of other methods for radioactive isotopes removal from aqueous solutions, such as solvent extraction and transport across liquid membranes with macrocyclic carriers.

In this thesis, the magnetic core/ion exchanger shell material was synthesized. Iron-(hydr)oxide particles have extremely large surface-to-mass ratios and are therefore considered to make up the largest fraction of the soils reactive surface area. Fe-(hydr)oxide particles are only a few nanometer in size when their surface-to-mass ratios are expressed as equivalent particle diameters. This suggests that Fe-(hydr)oxides are predominantly present as nano-sized particles. However, Fe-(hydr)oxides may aggregate or may be tightly attached to surfaces of larger particles. As a consequence, Fe-(hydr)oxides can have large surface-to-mass ratios without being present in the nanofraction.

In chapter 3 the experimental procedure is described. Synthesis procedure of magnetic nano-sized core/shell adsorbent is shown in scheme 3.1. In the chapter 3.2. there is a description of synthesized materials properties, i.e. microscope analysis SEM/EDS), dynamic light scatering (DLS), the chemisorption characteristic by Brunauer-Emmett-Teller (BET) method, Vibration Sample Magnetometer measurements (VSM), the analysis of X-rays (EDS and XRF) and zeta potential measurements.

In chapter 3.3 adsorption experiments procedure in batch conditions for cesium is presented. Author instead of radioactive isotopes, i.e. Cs-137 or Cs-134 used for adsorption natural cesium chloride, which contain 100% of stable Cs-133 isotope. It allowed to determine the concentration of cesium by atomic adsorption spectroscopy (AAS). Author has assumed that chemical properties of radioactive isotopes (Cs-134 and Cs-137) are the same as stable isotope Cs-133. It means that isotopic effect in case of Cs-137 and Cs-133 isotopes is negligible? Other problem connected with this methodology is total concentration of cesium in sorption experiments. Results of cesium adsorption shown in Fig. 4.38 informs that below cesium concentration equal to 80 mg/L there is no adsorption. On the other hand real concentration of cesium originated from Cs-137 is much lower (Cs-137 comes from nuclear fission and is carrier free. I expect that Mr. Liang Zhao explain these problems during the dissertation defense.

Results and their discussion is presented in chapter 4. First, $K_4[Fe(CN)_6]$ aqueous solution is added into the synthesized Fe(hydr) oxide. Next, the aqueous solution of $Co(NO_3)_2$ or $Cu(NO_3)_2$ or $Zn(NO_3)_2$ is added into this suspension. This core/shell materials were analyzed using SEM/EDS method allowed to determine the composition of ferrocyanides dotted with Co(II) or Cu(II) or Zn(II). But Author did not summarized contribution of elements in the core material. The sum of contributions was 95,49; 91,75 and 98,03 % for Co(II), Cu(II) and Zn(II) dotted ferrocyanides. Also composition of metals (K, Fe, Co or Cu or Zn) was calculated using XRF method. In this case the sum of contributions also was not calculated; my calculations give sums values below 100 %. My question is: how to explain these inaccuracies? In my opinion statistical error analysis should be done by Author. In chapter 4.2.3. there is magnetic characteristic of synthesized materials. VSM measurements show superparamagnetism of these materials. The size distribution of ferrocyanides was measured using DLS method and is shown in chapter 4.2.4. BET of chosen samples was determined using nitrogen gas adsorption at 77 K (chapter 4.2.5). Also X-ray diffractometry technology (XRD) (chapter 4.2.6) and zeta potential measurements (chapter 4.3.2) for chosen samples were applied.

Mr Liang Zhao also studied the adsorption of cesium cations from aqueous solutions (chapter 4.3). He determined:

- the influence of pH,
- the impact of adsorbent mass,
- the effect of contact time,
- the impact of cesium initial concentration,
- adsorption thermodynamics.

From Langmuir isotherm equation Author determined the maximum adsorption of studied materials as equal to 141 mg Cs^{+}/g. This means that sorbent possesses high adsorption capacity in comparison with commercial clay materials, carbon nanotubes or graphene oxide. Thermodynamic functions ΔH, ΔS and ΔG were calculated giving information that the cesium adsorption process is endothermic with positive entropy change. The question connected with cesium adsorption process is: in real coolant waters in case of their radiactive contamination there is not only cesium-137 and cesium-134 but mixture of different radioactive isotopes. For example: is this adsorption process selective for Cs^{+} against Sr^{2+} (Sr-90)? Author have not been studying in this dissertation the selectivity of cesium adsorption process.

Conclusions of dissertation, which are in chapter 4.3.7, should be given in extended form (2-3 pages) as separate chapter (no. 5). References are in separate chapter at the end of dissertation and contain 95 positions. The positions numbers should be extended in case of literature review (chapter 2). There is no literature positions of Author and Supervisor. For example the position: *A magnetic nanosorbent for cesium removal in aqueous solutions, Liang Zhao, Jakub Dudek, Halina Polkowska-Motrenko, Andrzej G. Chmielewski, Radiochimica Acta, Vol.104, Issue 6, pages 423–433, 2016*, is not cited in this dissertation.

This Ph.D. thesis do not contain English and Polish abstract of dissertation.

3. Specific comments

1. Problem of significant digits in numbers is not proper solved in this dissertation. For instance on page 49 numbers: 1.0249 0.04 and 1 possesses 5, 1 and 1 digits, respectively.
2. In page 9: instead of *radioactive elements* should be *radioactive isotopes.*
3. On page 9: instead of *Removal of the radioactivity from cesium-137* should be *Removal of radioactive cesium-137.*
4. In page 9: instead of *radioactivity* should be *radioactive substances.*
5. In page 9: instead of *allowing fast* should be *allowing efficient and fast.*
6. In page 11: instead of *coal and oil* should be *coal, oil and gas.*
7. In page 11: instead of *SOx, NOx* should be SO_x, NO_x.
8. In page 15: Table 1 – instead of *cesium in the thermal* should be *cesium isotopes in the thermal.*
9. On page 30: which cyanoferrates were used for cesium cations removal? Oxidation state of iron is here needed.
10. On page 33 and other: instead of NH_4OH should be $NH_3 \cdot H_2O$

11. On page 33 and other instead of *potassium copper hexacyanoferrate(II)* should be *potassium(I) copper(II) hexacyanoferrate(II)*.
12. On page 41: instead of $Cu(NO_3)_2$ *and* $Zn(NO_3)_2$ should be $Cu(NO_3)_2$ *or* $Zn(NO_3)_2$.
13. On page 52: instead of *heavy elements* should be *metals*.
14. On page 52 and other: instead of *is equal to 1,0.6 and 1* should be *is equal to 1.0, 0.6 and 1.0*, respectively.
15. On page 73 and other: cesium in aqueous solutions is in the form of cations, i.e. Cs^+. Everywhere instead of *cesium atom* should be *cesium cation*.

4. Conclusions

Despite of my critical remarks, Mr Liang Zhao has proved to be capable of solving chemical research problems. His doctoral thesis presents new results of scientific relevance. Mr Liang Zhao is coauthor of 8 publications in international scientific journals and 6 of them are related to his PhD topic. The PhD thesis satisfies the conditions of the Polish act on scientific degrees and academic title (*Ustawa o stopniach naukowych i tytule naukowym z 2003 r., Dz. U. Nr 65, poz. 595, ze zm. w Dz. U. z 2005 r. nr 164, poz. 1365)* and therefore

I recommend

Mr Liang Zhao thesis to be accepted by the Scientific Committee of the Institute of Nuclear Chemistry and Technology in Warszawa to be presented and defended.

September 1, 2016.