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THERMODYNAMIC BEHAVIOURS OF SELENIUM IONS ONTO BARRIER MATERIAL FOR NUCLEAR WASTE MANAGEMENT

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Abstract: In this study, modified bentonite was used as man-made barrier systems to investigate occurring reactions with interaction of ^{79}Se with barrier material systems to protect the environment from radioactive contamination. Thermodynamic parameters of interaction between dominant ion species of selenium and modified bentonite depend on contact time were investigated. In the interaction between modified bentonite and selenium, enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) were found to have different behaviours depending on the contact time. The adsorption enthalpy increases the duration of the endothermic reaction to the exothermic reaction one hour after the transition and endothermic reaction occurs after two hours.

Key words: Nuclear wastes, Man-made barriers, Modified bentonite, Selenium, Thermodynamic parameters

1. Introduction

For long-term storage of high level nuclear waste in geological repositories besides natural geologic barriers human made multiple-barrier systems are used to prevent dispersion of long-lived radioactive elements in waste to the surrounding environment in a probable accidental or unexpected situation. This type of barrier systems can stop long-lived radionuclides in waste before they arrive to earth's surface even if they disperse to the environment and prevent reaching of groundwater to waste. Therefore, it is necessary to have good knowledge about probable reactions in material after interaction of radionuclides with human made barrier materials (Bruggeman et al., 2005; Grambow, 2008).

Selenium (Se) is a very long-lived fission products and is one of the important redox sensitive elements in nuclear waste. There is not so much information about interaction of ^{79}Se which are very long-lived fission products with barrier materials (Jordan et al., 2009; Chen et al., 1999).

This study was aimed to determine thermodynamic behaviours of ^{79}Se on modified bentonite. Thermodynamic parameters such as enthalpy (ΔH), free energy change (ΔG) and entropy change (ΔS) of selenium adsorption were investigated from equilibrium adsorption data depend on contact time.

2. Materials and methods

The original selenium dioxide compound was irradiated in central irradiation tube of TRIGA Mark II nuclear reactor at Istanbul Technical University at 250 kW in 1 h. The stock solution of selenium(IV) (1780 mg/L) was prepared by dissolving appropriate amounts of irradiated selenium dioxide compound (SeO_2, Fluka, 99% purity) and used as radiotracer.

Batch experiments were carried out by using radioactive selenium solution satisfying liquid/solid ratio at different temperature and contact time. Data for thermodynamic studies were

obtained by determination of ^{75}Se radioactivity at high resolution gamma spectrometry system. In the measurements, adjusting the statistical confidence level to 1σ raises the accuracy of results. Counting time can be applied as 30 min related to the expected activity. The area of the peak in a gamma spectrum is a measure of the interested isotope resulting from interaction of gamma-radiation of corresponding energy in the radiation detector. Peak areas of ^{75}Se at 136 keV gamma-rays in the spectrums are determined by using nuclear analysis software programs. Calibration of gamma detection system is based on the rightly determination of net peak areas in the gamma-ray spectrum to the amounts of the elements present in the sample under studied experimental conditions. A standard point source such as ^{152}Eu is used in energy calibrations of the spectra.

In the adsorption process, the variation in thermodynamic parameters (ΔH, ΔS and ΔG) are very important to determine the spontaneity of adsorption process. ΔH, ΔS and ΔG parameters were obtained from adsorption experiment data in the temperature range of 273–323 K depend on time from 15 min to 240 min.

3. Results

To investigate the effect of temperature, the sorption of Se(IV) ions onto modified bentonite was studied in the temperature range of 273–323 K. The adsorption of Se(IV) on modified bentonite increased with increasing temperature till 1 h of contact time. This downtrend can be explained by the endothermic spontaneity of the Se(IV) adsorption. After 1 h of contact time, the adsorption of Se(IV) on modified bentonite was decreased with increasing temperature by the exothermic spontaneity. Uptrend changed after 2 h of contact time which indicate that the Se(IV) adsorption process was endothermic.

A similar trend was observed for Gibbs free energy. The Gibbs free energy values, which are positive for short periods of time, turn negative Gibbs free energy value as a result of the contact time of 45 min. After 3 hours, the Gibbs free energy value is again positive.

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ТЕРМОДИНАМИЧЕСКОЕ ПОВЕДЕНИЕ ИОНОВ СЕЛЕНА НА БАРЬЕРНЫЙ МАТЕРИАЛ ДЛЯ ОБРАЩЕНИЯ С ЯДЕРНЫМИ ОТХОДАМИ

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Резюме: В этом исследовании модифицированный бентонит был использован в качестве искусственных барьерных систем для изучения происходящих реакций при взаимодействии ^{79}Se с системами барьерных материалов для защиты окружающей среды от радиоактивного загрязнения. Изучены термодинамические параметры взаимодействия доминирующих видов ионов селена и

модифицированного бентонита в зависимости от времени контакта. Взаимодействие между модифицированным бентонитом и селеном показало, что энтальпия (ΔH), энтропия (ΔS) и свободная энергия Гиббса (ΔG) имеют различное поведение в зависимости от времени контакта. Энтальпия адсорбции увеличивает продолжительность эндотермической реакции до экзотермической реакции через один час после перехода, а эндотермическая реакция происходит через два часа.

Ключевые слова: ядерные отходы, искусственные барьеры, модифицированный бентонит, селен, термодинамические параметры.

NÜVƏ TULLANTILARININ İDARƏ OLUNMASI ÜÇÜN BARYER MATERİALINA SELENYUM İONLARININ TERMODİNAMİK TƏSİRİ

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Xülasə: Təqdim olunan məqalədə, ətraf mühitin radioaktiv çirklənmədən qorunması üçün baryer material sistemləri ilə ^{79}Se'nin qarşılıqlı təsirindən baş verən reaksiyaları araşdırmaq üçün süni baryer sistemləri kimi modifikasiya olunmuş bentonit istifadə olunmuşdur. Selenyumun dominant ion növləri ilə kontakt müddətindən asılı olan modifikasiya olunmuş bentonit arasındakı qarşılıqlı əlaqənin termodinamik parametrləri araşdırılmışdır. Müəyyən edilmişdir ki, modifikasiya olunmuş bentonit və selenyum arasındakı qarşılıqlı əlaqə zamanı entalpiya (ΔH), entropiya (ΔS), Gibbs azad enerjisi (ΔG) kontakt müddətindən asılı olaraq müxtəlif təbiətlərə malik olurlar. Adsorbsiya entalpiyası keçiddən bir saat sonra endotermik reaksiya müddətini ekzotermik reaksiya müddətinə artırır və endotermik reaksiya iki saatdan sonra baş verir.

Açar sözlər: nüvə tullantıları, süni baryerlər, modifikasiya olunmuş bentonit, selenyum, termodinamik parametrlər