sorption behavior of some fission products on iron(3) silicate as inorganicion exchange material

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The growth of nuclear energy industry as well as the increased use of radionuclides in peaceful uses of atomic energy added considerable amounts of radioactive materials to our environment, such as CC, Nat Co2+ and Ce3t. The main methods which are currently used for the treatment of radioactive waste solutions are chemical precipitation adsorption and ion exchange process. Choice of certain techniques is governed by radiochemical composition of waste to be treated as well as the economic aspects. The potential usefulness of inorganic ion exchangers has been proved in the preparation and fixation of fission products and extrudes.This work has been done in an attempt to prepare inorganic ion exchangers as a cation matrix that can be of help in nuclear waste problem. This work is directed to the preparation of iron (III) silicates as a cation exchange in different operative conditions which among several new synthetic ion exchange materials, double salts of polybasic acids is very promising. In this concern, kinetic studies, distribution coefficients adsorption isotherms as well as column studies are investigated as applied part on the separation of CC, Nat, Co2+ and Ce3t, on both forms of iron silicate to optimize the operative conditions for the removal of these aforementioned from the back end of nuclear fuel cycle.The work carried out in this thesis is summarized into three main chapters, namely, introduction, experimental and finally results and discussion.First chapterThe first chapter, introduction, includes abrief account on history, comparison of the properties of organic and inorganic ion exchangers, classification of inorganic ion exchangers, chemical, thermal and radiationM.Khahl - - M.Sc.ChemistrySUMMARYstabilities of inorganic ion exchangers, ion exchange theory , ion exchanger regeneration, applications of inorganic ion exchangers and new developments in ion-exchange materials. A literature survey related to the different inorganic ion exchangers, phosphates, arsenates, titanates, antimonates, molybdates and silicates as well as iron silicates for separation and preconcentration of certain radionuclides of importance in nuclear technology since 1960 up to 2006 is reviewed.Second chapterThe second chapter, experimental, deals with the different materials employed and their chemical purity, as well as the methods utilized for the preparation of the radioactive materials was given. Detailed descriptions of the instrumentations, the analytical techniques and procedures used in this thesis were also detailed. A detailed description of the method of preparation of iron silicates (FeSi-I, FeSi-II and

FeSI-III) at different operative conditions and set up used in this work were presented. Column chromatographic techniques which used as applied part for this work was also described.Third chapterThe third chapter deals with the results and discussion and is divided into five main sections:Preparation and Characterization of Iron (III) SilicateThe Na’ form of iron (III) silicate as a cation exchange materials were prepared by adding equimolar solution of iron trichloride to sodium silicate to obtain different Fe/Si molar ratios of 1.0, 0.5 and 2.0 for FeSi-I, FeSi-II and FeSi-III, respectively. All samples of iron silicates (FeSi-I, FeSi-II and FeSi- III) were hard granulates in nature and suitable to use in packed column No changes in particle diameters of iron silicate samples are observed with increasing the heating temperatures up to 850°C.M.Khalil 118 - M.Sc.ChemistrySUMMARYPhysicochemical properties of the prepared materials of iron silicate (FeSi-I, FeSi-II and FeSi-III) were identified by using different techniques, such as, chemical stability, IR-spectra, XRF, X-Ray diffraction patterns as well as thermal analysis TG and DTA.The chemical stability of the prepared iron silicate samples (FeSi-I, FeSi-II and FeSi-III) was investigated in water, nitric and hydrochloric acids at different concentrations (0.1, 0.5, 1.0, 2.0, and 3.0M acid). The prepared materials are stable in water and low concentrations of acid up to 1M. While, the samples are partially dissolved in 3M acid and completely dissolved at 4M acid. As far as the chemical stability of the prepared samples with respect to the composition of the materials is concerned. -The solubility of the prepared iron silicates follows the order;FeSi-III > FeSi-I > FeSi IIwhere the solubility of the prepared materials is increased with increasing Fe/Si molar ratios.The spectrum of prepared iron silicates (FeSi-I, FeSi-II and FeSi-III) were displayed in the IR range 400-4000 cm-I using 1(13r disc technique. The IR spectra of different samples are nearly has the same spectrum with slightly differ in details and this is may be due to the difference in the preparation condition and surface structure between the ratios of iron silicate samples.X-ray diffraction patterns of the prepared iron silicate samples (FeSi-I, FeSi-II and FeSi-III) at different drying temperatures (50, 200, 400, 600 and 850°C) are discussed. It is found that all the prepared samples are clearly amorphous materials at all conditions studied, and there is no change in the structure of prepared materials with increasing the dryingtemperature up to 850 C.The DTA-TG thermal analyses of iron silicate for the differentM.1Chali1 119 - M.Sc.ChemistrySUMMARYprepared forms (FeSi-I, FeSi-II and FeSi-III) are investigated. from the DTA/TG analysis of FeSi-I, -II, and -III forms and it can be concluded that the all forms show high thermal stability up to studied -temperature (1000°C) and the trend of the water ratio contents take the order;FeSi FeSi-I > FeSi-IIIThis may be due to the increase of acidities of materials II (14.75%) with increasing the silicon species which may leads to the increase of electrostatic interaction of the counter ions with the exchange sites. The ion exchange capacity of the different studied cations are slightly decreases by increasing the drying temperatures from 50 to 200 °C followed by fast decrease with continuous heating up to 850 °C and no drastic change occurs in the surface structure and X- ray diffractions, because loss of theM.Khalil M.Sc.ChemistrySUMMARYfree water which may act as the exchange sites.Distribution InvestigationThe potential use of the prepared ion silicate in separation of some radioactive nuclides involving cesium, sodium , cobalt and cerium ions were studied in order to asses and evaluate the prepared materials for separations. The distribution coefficients for all metal ion studied at different conditions were increased with increasing the pH of solutions.The plots of log Kd at infinitesimal exchange (Cs+, Nat Co2+ and Ce3+) Vs. pH of solutions are shown a linear relationship with slope smaller than the valence of the studied cations were obtained indicating the ion exchange reaction deviated from the ideality process, the sorption behavior of ions increase with increasing the reaction temperature from 25 to 65 ±1°C, which revealed that all these systems are endothermic process and the selectivity sequence was in the order;Cs+ > Ce3+ > Co2+ > Na+The effect of y- radiation on FeSi-II was studied and it is seen that the values of distribution coefficient is slightly affected and the affected of y- radiation on FeSi-II can be neglected. We can emphasize that fairly good resistance of iron silicate (FeSi-II) as acation exchanger against y-radiation in the range investigated.Kinetic StudiesThe conditions of the present thesis were set to study the particle diffusion mechanism only, as the limited batch technique was employed. The study of the effect of concentration on the rate of ion exchange of Cs+Na+ and Co2+/Na+ exchange an both ratios of FeSi-I and FeSi-II at 25±1°C as a relation between F and t at different concentration of metal ions. At concentration 5x10-3 the rate of exchange is independent of the metal ion concentrations. Particle diffusion control at such concentrationsMIChalil - 121 M.Se.ChemistrySUMMARY5x10-3M) is the main mechanism. Values of effective diffusion coefficient (D1) of Cs+ and Co2+ ions at different particle diameters are calculated. Furthermore, since the diffusion coefficient Di of the metal ions studied are independent on the concentrations of the metal ions in solution and the mechanism of the diffusion of these ions in the prepared materials is considered to be unchanged by the composition of the materials, and the exchange rate of Cs+ and Co2+ is increasing with decreasing in particle diameters of the material. This indicates that under these conditions, the rate determining step is diffusion through the exchanger particles and this observation is agree with the fundamental theory of particle diffusion mechanism.The values of kinetic and thermodynamic parameters such as effective diffusion coefficient (D1) energy of activation (Ea) and entropy of activation (AS*) for the studied cations Cs+ and Co2+ ions on prepared iron silicate (FeSi-I and FeSi-II) at 25, 45 and 65±1°C are calculated. It is clear that the rate of reaction is increased with increasing the reaction temperature from 25 to 65±1°C. This may be due to increasing the mobility of ions with increasing the reaction temperature.Negative values of AS* for Cs+/Na+ and Co2+/Na+ exchange systems on iron silicate heated at different drying temperatures have been obtained at all condition studies. Negative values of entropy of activation AS* have been reported on the prepared matrices at different conditions. In general, negative values of AS* are common in ion exchange process. The negative values of AS* indicate that as a result of exchange no significant change occur in the internal structure of iron silicate.Sorption IsothermsThe adsorption of Na+, Cs+ and Co2+ ions in the range of con-centrations (5x10-4-10-2M) at different reaction temperatures, 25, 45 andM.Khalil - 122 M.Sc.ChemistrySUMMARY65 +1 °C on prepared iron silicates is found quite fit with Langmiur plots. The relation between equilibrium concentration of ions/ amount of adsorbed ions against the equilibrium concentration of studied cations Nat Cs+ and Co2+ on both ratios of iron silicates are linear relations and these linearity are quit fit well with the Langmuir adsorption isotherms over the entire range of the studied concentrations.from above results, we can declare that sorption of studied cations (NatCs+ and Co2+) on both (FeSi-I and FeSi-II) is chemically adsorbed. 3.6. Column OperationsThe main theory which explains separation by column chromatography is plate theory. Investigation were conducted to explore suitable conditions for quantitative loading and sorption of CC, Na+ and Co2+ in nitrate media by chromatographic column procedures at room temperatures (25). As far as the break-throurh capacity of the column for 134Cs, 22Na and 60c0 radionucldes (10-3M for each) from FeSi-II column in the feed solutions.It is found that the selectivity of the ions towards the FeSi-II is in the order;CC > Co2+ > Na+and the break-through capacity for all the metal ions studied are calculated and it found to be 0.35, 0.33 and 0.15 meq./g for CC, Co2+ and Na+ respectively.The elution profile for the investigated cation Cs+, Co2+ and Na+ ions are studied in nitric acid solutions [0.01-1M].from the presented results. It is clear that the different ions can separately from FeSi-II column by 0.01 M HNO3 and it is found that the tail of different ions is continuous until the volume of eluent around 50 ml and it is removed adsorbed ion completely (100%), so we can using the column in the regeneration process.M.Khalil - 123 M.Sc.Chemistry