

Computer Modeling and Laboratory Experiments to Design Sorbents for Remediating Radiologically Contaminated Soil and Water: Nanoscale Structured Surface Layers

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Abstract-This research illustrates the application of a combination of computer modeling and laboratory experiments to designing nanoscale structural surface layers of compositions for remediating radiologically contaminated soil and water. Natural sorbents and sorption materials with nanoscale structured surface layers of various structures are compared in terms of sorption efficiencies. Monte Carlo simulation to generate numerical calculations and chemical and physical analyses to verify the modeling predictions of the structure of metallic surface zones synthesized by ionic beams was performed. Fe, Al, and Al₂O₃ compositions were irradiated with Ti ions to form nanoscale structured surface layers of various structures. ⁹⁰Sr and ¹³⁷Cs were used in the laboratory experiments to assess sorbent performance. The results demonstrate that using the sorbents with new structural forms of a surface produces increased efficiency in potential radionuclide sorption.

Keywords- Ionizing Fluxes; Radiation Factor; Materials Science; Modeling; Natural Sorbents; Nano Structured Surfaces; Synthesized Compositions; Soil Solutions

I. INTRODUCTION

Environmental remediation of aquatic and terrestrial sites that have been contaminated by varying levels of radioactivity increasingly is done using various kinds of natural sorbents. Using sorbents to remediate contaminated sites is attractive because a number of radionuclides such as ¹³⁷Cs and ⁹⁰Sr have relatively long half-lives, exhibit water solubility, and can be readily incorporated into the soil or water media ^[1]. As a result, the effectiveness and efficiency of sorption materials for the remediation of contaminated sites and disposal of radioactive wastes is a significant issue. Although natural sorbents can be effective, they typically exhibit low sorption efficiency. This deficiency underscores the need to develop new material structures for use as sorbents that are capable of functioning with greater efficiency. Prior research has examined innovative structural forms that exhibit increased sorption properties ^[2, 3]. For example, the synthesis of simulated nanoscale structured metallic compositions (e.g., iron [Fe], aluminum [Al] and aluminum oxides) by manipulating molecular interactions to create materials with enhanced sorbent characteristics has been investigated. Those preliminary studies raise the question of the importance of

being able to adjust the size and structural form of a surface, including particles, grains and crystals. They also underscore that, in designing and producing these enhanced sorbents, it also is essential to bear in mind radiation factor impacts on sorbent properties ^[4, 6].

Computer modeling in combination with laboratory experimentation provides a viable empirical approach to elucidate the influence of ionizing fluxes on synthesized compositions created using nanoscale structural surface layers. This study is devoted to using those tools to evaluate designing and synthesizing new sorption materials with nanoscale structured surface layers of various compositions of Al and Fe including oxides ^[7-9]. By varying structural forms and compositions, the computer simulations and laboratory experiments provide insights into the ability of nanoscale structures to increase sorption reactions by enhancing their physical and chemical properties (e.g., ability to form new compositions, build new structural forms, and cluster).

II. METHODS

The computer modeling portion of this research used Monte Carlo simulation to create new nanoscale metallic structures and assess their sorption performance. The Monte Carlo method using the program SCATTER ^[5] for the modeling description of ion interaction with substance by binary impacts was used for this simulation. The interaction effects and as stopping of incident particles at elastic and inelastic collisions, scattering inside iron samples, defect generation, particle reflections from the target as well as its dispersion by both incident and reflected particles were estimated according to the software program SCATTER of the study ^[8].

The laboratory experimentation phase was used to validate the computer modeling predictions. For that portion of this research, plasma technology was used to create Fe, Al, and aluminum oxide (Al₂O₃) compositions with nanoscale structured surface layers of various structures ^[2, 7]. Ionic plasma synthesis on exposure to cryogenic plasma streams of zirconium (Zr) and titanium (Ti) on Fe and Al respectively was used for formation of the compositions

selected for evaluation. Prior to creating the structures, the input materials were polished and purified to remove oxide skin and other contaminants before subjecting the input materials to ionic irradiation. The ionic irradiation was carried out in a vacuum chamber ($5 \cdot 10^{-6}$ mm Hg) at ion energy values from 0.1 to 2.0 keV. The structure and properties of the synthesized compositions were determined using multiple methods of physical and chemical analysis, including X-ray phase, local X-ray spectrum, micro durometric analysis, nuclear gamma resonance (NGR), and electronic microscopy.

III. RESULTS

This section summarizes the results of the computer modeling using Monte Carlo simulation to generate numerical calculations and the empirical analysis of the structure of metallic surface zones synthesized by ionic beams.

A. Monte Carlo Modeling

The first stage of this research employed Monte Carlo modeling to test the theoretical assumptions about the formation process of the nano compositions based on the interaction of plasma streams with Al and Ti for varying

TABLE I EMBEDDING DEPTH IN FE FOR TI IONS AT VARIOUS INFLUENCE MODES, 10^{-8} M

Plasma Charge	Embedding Depth for Ion Energy of 1000 eV	Embedding Depth for Ion Energy of 2000 eV
+1	0.35	0.93
+2	0.92	2.60
+3	1.73	4.70
+4	2.60	7.50

Fig. 1 presents a graphical depiction of the results of the Monte Carlo simulation used to calculate the distribution of Ti ions by embedding depth in Fe as a function of the initial energy stream using a binary collision model for the interaction of Ti ions with Fe. The initial energy stream

plasma charges and embedding depth for ion energy. In order to illustrate the results, we focus this portion of the paper on discussing the results for simulating the imbedding of Ti ions in Fe to form a nanoscale metallic composition.

Table 1 shows the calculations generated predicting possible penetration depth into Fe for 100 eV and 2000 eV for plasma charges of +1, +2, +3, and +4 for the direct "embedding" of ions of multi-charge plasma of Ti. Table 1 reveals that holding the plasma charge constant and doubling the ion energy are estimated to produce a substantial enhancement in terms of embedding depth. When the plasma charge = +1 the embedding depth increases by a factor of 2.66, by a factor of 2.83 for plasma charge = +2, by a factor of 2.72 for plasma charge = +3, and by a factor of 2.88 for plasma charge = +4 shifting from an ion energy level of 1000 eV to 2000 eV. Holding the ion energy constant at either 1000 eV or 2000 eV and increasing the plasma charge assumed as an input value for the computer simulations similarly is predicted to enhance embedding depth for these compositions. As a result, increasing both the plasma charge and ion energy is predicted to produce structures with the greatest depth of embedding Fe in Ti, with a +4 plasma charge and 2000 eV ion energy estimated to result in an embedding depth of 7.50.

evaluated in this study ranges from 300 eV to 1500 eV. At the same time, the calculation of parameters of this process was carried out by the Monte Carlo method using the binary collision model as the interaction modeling of ions with substance. The calculations predict the process of interaction of ions with a target depends on both the value of stream energy and the specific irradiated metal. The most probable penetration depth of Ti ions in Fe increases nonlinearly as the initial energy increases and peaks at approximately 10×10^{-8} m and then decreases rapidly. Thus, the relative half-width of the distribution quickly increases with the corresponding energy growth for Ti. For the energy range used in this simulation, Ti ion penetration into Fe surface layers average between 300 to 600 nanometers. The computer modeling results support the conclusion that binding structural surface layers can create nanoscale compositions.

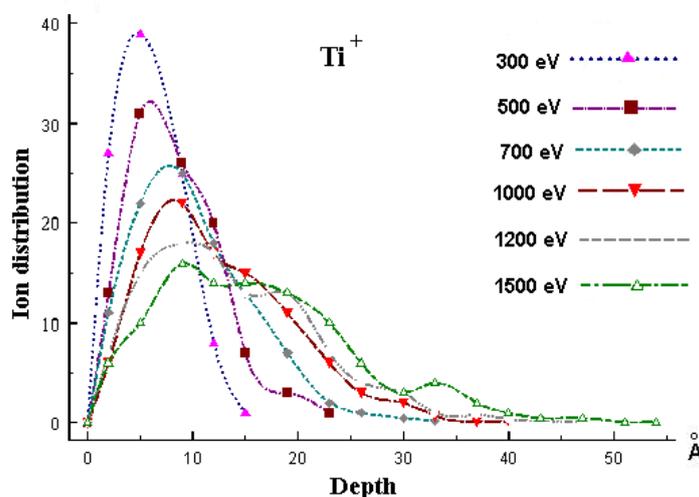


Fig. 1 Cross-section of embedding of Ti ions in Fe as function of the initial stream energy

B. Experimental Analysis

The second stage of this research employed a series of laboratory experiments conducted in order to evaluate the surface layers associated with the nanoscale structures synthesized by ionic beams. The experiments produce empirical results consistent with the Monte Carlo modeling predictions. Taken as a whole, the chemical and physical analyses confirmed displacement of the Fe atoms by the Ti ions results Fe dispersion, Ti concentration on a surface, and their mutual hashing that can be used at the composition formation to create new structural forms of sorption material surfaces.

Fig. 2 shows that the structure of surface zones synthesized by ionic beams depends on both the basic metal of the target and the metal of an ionic beam. Comparing the structure of Fe and Al or carbon (C) and Al₂O₃ surfaces after impact of Ti ionic beams reveals distinct differences in hard-grained structure and density. Moreover, the sedimentation pattern for C and Al₂O₃ impacted by Ti ions is less dense when compared to the sedimentation pattern obtained for either Al or Fe. Thus, the laboratory experiments confirm that formation of the distinct metallic structures observed under experimental conditions is a function of differentials in the energy transferred from ionic beams to atoms in a crystal lattice of metal during the irradiation process thereby influencing the nanoscale structure of surface zones.

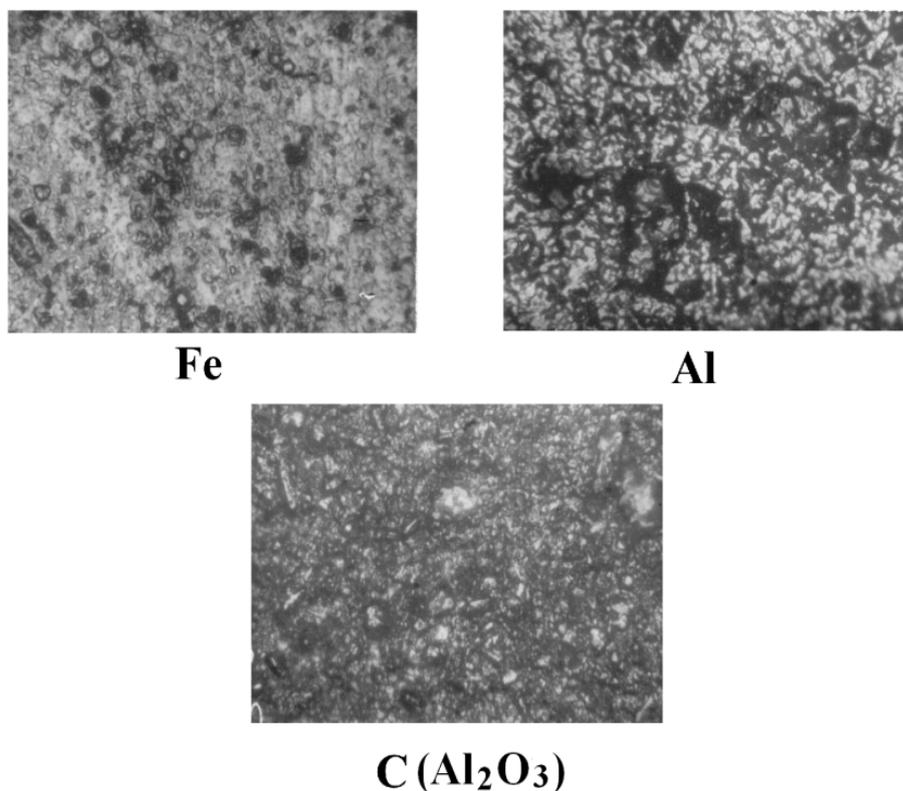


Fig. 2 Micro structure of surface zones synthesized in various metallic materials, magnification x 500

Local X-ray spectrum analysis was used to investigate the distribution of Ti on Fe surface and in surface zones. Measurements indicated that the range for zone width of the modified structure in both Fe and Al was from 5 to 10 microns (μ). The range for zone width for Al₂O₃ was reduced up to 2-3 μ less.

NGR-spectroscopy revealed spectra of surface zones represented the well-solved Zeeman sextets for characterizing nanocrystalline structure formation [10, 11]. The additional fine structure of spectrum caused clusters of Ti atoms is shown on Fig. 3.

The macro clusters of Ti shown on Fig. 4 (white color) were marked on the samples by means of the local X-ray spectrum analysis.

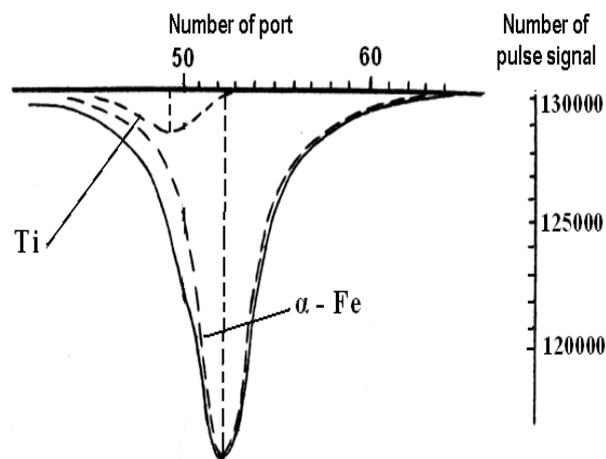


Fig. 3 NGR-spectra (fragment) of iron surface after irradiation of Ti ions

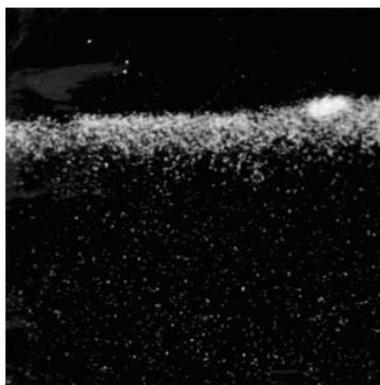


Fig. 4 Ti clustering on surface zones of compositions with Fe base, magnification x 1000

X-ray phase analysis confirmed that the structure of surface zones of Fe and Al was composed of oversaturated solid solutions of Ti in Fe and Laves phases such as $TiFe_2$. Table 2 summarizes the chemical structure and properties of the base material and characteristics of the surface zones investigated. The accuracy of these results was confirmed by also investigating the structure of surface zones using electronic microscopy in addition to the x-ray phase analysis. The size of particles that formed intermetallics (e.g., a class of metallic materials that form ordered crystal structures) such as $TiFe_2$ was found on the average to be in the 100-700 nm range.

TABLE II CHARACTERISTICS OF SURFACE ZONES SYNTHESIZED IN FE AND AL

Chemical Structure of Base Material, Mass%	Properties of Base Material		Properties of surface zones		Width of α -Zone, μm
	Phase Structure	Lattice Period α -Fe, nm	Phase Structure	Lattice Period α -Fe, nm	
Fe - 100%	α -Fe	0.2867	α -Fe, α -Ti, Fe_2Ti	0.2863	9-10
Al - 100%			Al, α -Ti, Al_2Ti		5-6
Al_2O_3			Al_2O_3 , α -Ti, Al_2Ti		2-3

The next step in the experiments involved the use of micro durometric analysis. Micro durometric analysis was employed using samples of the Fe and Ti compositions to evaluate micro hardness of a surface. The structure of the synthesized surfaces exhibited increased mechanical properties. For example, the surface zones synthesized in Fe had higher values of micro-hardness on Vickers (H_V); both an initial condition (1200-1500 MPa) and an increased temperature of 700-1000⁰C (1000-1450 MPa) in comparison with initial Fe (600 MPa), Al and its oxides. Similar increases in surface hardness at the formation of compositions on the basis of Al and oxides also were demonstrated in the experiments.

The final portion of the laboratory experiments involved an evaluation of the sorption properties of the synthesized compositions. In this step, the decrease in ⁹⁰Sr and ¹³⁷Cs radioactivity in soil solutions using an Al_2O_3 sorbent was compared to the results using a composite sorbent. For this purpose, aliquot solutions in volume of 10-25 ml were selected. The measurements of specific activity were carried out before and after the introduction of Al_2O_3 sorbents in active solutions, as well as before and after the introduction of composite sorbents on the basis of Al_2O_3 with the new nano structured form of a surface. Fig. 5 shows the plot of sorption ability K . The graph indicates the change in activity for each radionuclide in relation to its alimentation in the liquid phase. The results demonstrate that the synthesized sorbents increased radiological decontamination efficiency

on the average by 1.2 to 2.5 times in comparison with Al_2O_3 .

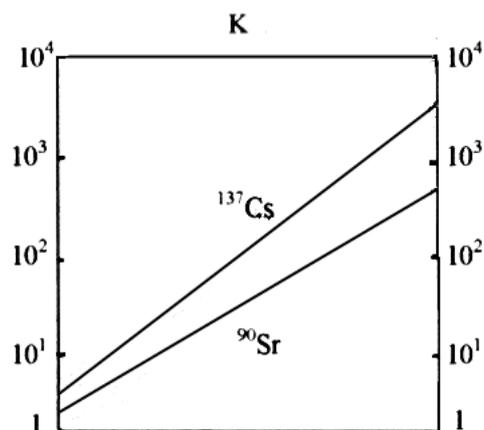


Fig. 5 Modeling activity decrease in soil solutions (on the left for Al_2O_3 sorbent, on the right - for composite sorbents)

IV. CONCLUSION

This research demonstrates that designing and producing sorbents with nanoscale structural forms of surfaces provides an opportunity to increase the efficiency of radionuclide sedimentation. The results of the Monte Carlo simulation when combined with a series laboratory experiments which offer verification that sorbents with new structural forms of a surface—including nanoscale structured intermetallics with enhanced chemical and physical properties—have increased sorption efficiency. Because the composite sorbents with nanoscale surfaces exhibited radiological decontamination efficiency on the average 1.2 to 2.5 times better than the control sorbents, it is likely further laboratory experimentation and pilot-scale field tests investigating an expanded range of both

nanocrystalline structure sorbents and precipitable radionuclides will accelerate the remediation of radiologically contaminated soil and water.

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