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学位論文題目	Adsorption Characterization by Water-Rock Interaction Experiment with Weathered Pumice Tuff from a Radioactive Waste Repository (放射性廃棄物処分場における風化軽石質凝灰岩の水－岩石反応実験からみた吸着特性評価)
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論文の内容の要旨

Geological materials in the sub-surface are frequently participating in different water-rock interactions with the surrounding ground water. In long geologic time, such interactions may have significant influence on the properties of rocks and changing their natural behavior. Investigating those behaviors surrounding a radioactive waste repository is particularly important to the fact that migration of hazardous radionuclides is extremely critical issue for the countries who use nuclear energy.

Long term weathering processes in the geosphere surrounding the repository by contacting the surface/subsurface water can lead to the formation of redox front zone. This zone might have significant effect on the adsorption of certain nuclides that could be released from the radioactive wastes. In recent years, adsorption characteristics of radionuclides in such oxidizing or reducing conditions have gained interest because of frequent presence of such environment in the subsurface where ground water-rock interaction occurs.

Cesium (Cs) and strontium (Sr), which are common non-redox-sensitive elements released from radioactive wastes, are widely used for the performance assessment of a waste repository. Among several potential host rocks, pumice tuff is already been selected for hosting low and intermediate level radioactive wastes in Japan. However, the pumice tuff formation was found to be affected by redox zone. In the present study, water-rock interaction with such redox affected pumice tuff was investigated using Cs and Sr.

Conventional batch sorption study was opted for determining sorption coefficients which is one of the most import-

ant water-rock interactions. Comparison was made between fresh and oxidized tuff in terms of their natural dissolution, adsorption behavior, pore properties etc. While comparing, proposal was given to use a particular shaped intact solid to obtain *in-situ* field condition. Prior to the specific experiments, pumice tuff was characterized in detail with several analytical techniques, to find out the potential parameters influencing adsorption behavior. Although fresh and oxidized part of the pumice tuff was clearly distinguishable in naked eye, mineralogical and chemical properties did not show considerable variation. However, pore properties significantly varied between them which were assumed to be the main factor affecting the adsorption property.

From all the investigations, important outcomes can be summarized as follows.

Strontium is an element that can readily dissolve in groundwater under oxidizing conditions. Furthermore, the host rock accelerates the dissolution, which might exceed the adsorption quantity at low initial Sr concentration, affecting the adsorption significantly. It has been observed that the threshold concentration between adsorption and dissolution lies between 10^{-4} and 10^{-5} mol/l for the case of the studied rhyolitic pumice tuff. Below 10^{-5} mol/l Sr concentration, adsorption quantity was significantly affected by the dissolved Sr concentration in oxidized pumice tuff. The *in-situ* nuclide concentration is thus suggested to incorporate in the existing K_d calculation procedure to obtain precise adsorption quantity of any nuclide. Such consideration is imperative if the solid phase is affected by oxidizing or reducing condition. Those weathering condition can accelerate the natural dissolution reaction and increase the hazardous nuclides in the groundwater and in consequence, reduce the adsorption capacity. Without considering the dissolved concentration of target elements, especially which are abundant like strontium, the results of adsorption coefficient values might be misleading.

Adsorption behavior of pumice tuff was found largely dependent on ionic strength i.e. salt concentration of the ground water. The cations present in the water can participate in sorption reaction either by ion-exchange or by creating new complex. It was observed that with salt concentration and adsorption quantity are inversely proportional to each other and with decreasing salt concentration, the effect becomes more noticeable. Initial concentration effect on adsorption was found negligible; however, they might be visible at extremely low concentration. pH dependency from the experimental results was not significant, although model simulation indicated that there might be considerable dependency at low pH condition. No significant differences were observed due to oxidation of pumice tuff at high initial concentration and high ionic strength, however, at low Cs concentrations of 10^{-6} and 10^{-7} mol/l, and low ionic strength (less than 1.0 mol/l), marginally decreased sorption was observed in oxidized tuff. This is due to the smaller amount of pore area in oxidized tuff resulted from the less number of smaller pores and destruction of available surface area by oxidation. For both Cs and Sr, ionic strength more than 1.0 mol/l and initial concentration of 10^{-4} mol/l were found to be the critical concentration where no experimental factors were found effective on adsorption. More than 10^{-4} mol/l Cs or Sr concentration were found to provide extremely low sorption coefficient due to more than saturation concentration. High ionic strength condition was successfully used in the surface complexation model which provided comparative sorption parameters with previous studies. Inversely proportional ionic strength dependency and negligible initial concentration or pH dependency were evident for the pumice tuff, which are more apparent in oxidized part at ionic strength less than 1.0 mol/l and initial concentration less than 10^{-5} mol/l.

Block shaped intact samples for conventional batch sorption study were used to investigate the relation of pore properties to the adsorption of Cs. Intact samples exhibit *in-situ* pore properties in terms of pore area and surface area. The change of pore properties change due to oxidation was found significant as the pore area and surface area reduced considerably which should affect the sorption quantity. Although K_d values in oxidized tuff did not show large difference comparing to fresh part, the suitable surface sites should allow noticeable difference in K_d on varying surface area. Adsorption did not affect the pore characteristics; rather pores were assumed to be affected due to long aging period and oxidizing condition which affected the sorption mechanism. Due to oxidation, total pore area, surface area or specific surface has reduced significantly although porosity remained similar. Reduction of micropores of less than 3.3 micrometer size was found to be responsible for reducing those parameters. ‘Generation of new surface area due to weathering’ was not found applicable for the present case because of absence of appropriate mineral phase in initial condition. The relation of pore properties with adsorption was not clear from the fresh tuff, however, oxidized part showed some positive correlation among pore area, surface area and sorption coefficients. Oxidation phenomena have made the increasing trend of sorption coefficients clearer with pore or surface area increase. The oxidation phenomena have made those changes more evident. As there were negligible chemical or mineralogical variation between fresh and oxidized pumice tuffs, changes in pore size distribution was found to be the key parameter to affect adsorption behavior. Especially, ‘reduction of micropores less than 0.33 μm size due to oxidation which resulted in reducing specific surface area into half’ were confirmed to be the main factor affecting water-rock interactions. However, if the changes in pore properties would be constant, geochemical parameters could influence the adsorption behavior significantly.

Cubic block shaped intact samples were successfully used to determine distribution coefficient, K_d of cesium and strontium on fresh and oxidized pumice tuff. The K_d values were compared with the powder samples under similar experimental condition. Intact samples from fresh tuff showed less than one order smaller values, which increased to more than one order in oxidized tuff which is comparable with literature. Therefore, use of block samples was proposed as alternate of powder in the batch experiment. However, this may apply for pumice tuff like highly porous and permeable solid phase. Experiment with more samples with variable geochemical condition should be conducted to confirm use of block samples as intact solid as alternate of powder materials.

Finally, it can be stated that although Cs and Sr are non-redox sensitive, some variation of their natural behavior were observed in the oxidized pumice tuff. However, instead of alteration of elemental behavior, it’s the rock properties which were changed due to oxidation and that forced to change the elemental activities. Therefore, weathered condition of pumice tuff or other geological materials should be considered during any water-rock interaction study.

論文の審査結果の要旨

当学位論文審査委員会は、Mohammad RAJIB 氏の提出した学位論文について、平成 28 年 7 月 28 日に公開で論文発表会を開催し、論文内容の審査を行った。審査結果を以下に要約する。

本論文は、放射性廃棄物処分時における核種の収着現象について、岩石の風化（とくに酸化・溶解）の影響と水－岩石相互作用の観点から実験を行い解析したものである。軽石凝灰岩を母岩とする地域を事例とし、地中浅部における岩石の化学状態の違いが、安定核種 Cs（セシウム）および Sr（ストロンチウム）の収着分配係数に与える影響を定量的に検討した。

第 1 章では、問題提起として、放射性廃棄物処分は長期間にわたり考慮しなければならない地球表層の地形・地質の変化に関する詳細な調査の必要性が説かれている。すなわち、処分期間における埋設候補地材料としての母岩の状態変化、とりわけ風化が、収着特性に与える影響を考慮することが重要であることが指摘されている。風化前後の試料を用いた水－岩石相互実験を行い、溶液側・固相側双方の精密な分析を行うことで、課題解決の可能性を述べている。

第 2 章では、この分野に関する文献調査を詳細に行い、1) 特に Cs と Sr に関する研究例、2) 種々の実験的手法のレビュー、3) 未風化部と風化部における物性（特に間隙物性）の違いに関する研究例について整理した。そのうえで、処分場の工学的性能および長期安定性評価の観点からも、処分場の基盤をなす母岩の風化状態の違いによる核種の収着特性の違いを、溶解と吸着挙動まで掘り下げて調べることの重要性について指摘した。

第 3 章では、試料の性状と予備分析の結果について述べられている。試料を採取した地域について地質学的観点からの観察が行われ、採取地点を取り巻く露頭の状況が詳細に記述された。採取した岩石試料は、多孔質性の軽石混じり凝灰岩であり、風化部分と未風化部分は色調の違いにより目視で区別することができること、地球表層で気体およびその影響を受けた地下水と接触した岩石であれば普遍的に見られる材料であること、が確認された。

第 4 章では、実験用に入手した岩石試料に対し、未風化部と風化部とに分別した上で、詳細な分析・測定、および水－岩石反応実験がなされたことについて述べられている。まず、X 線分析法（XRD、XRF）および走査電子顕微鏡（SEM-EDS）を用いて、鉱物同定と化学組成分析がなされ、さらに水銀圧入法（MIP）により比表面積等の間隙物性が評価された。

第 5 章では、各種試験の結果が記されている。風化部分で Fe（鉄）と S（硫黄）の含有濃度が高いこと除き、風化前後で鉱物種および化学組成は類似していることが明らかにされた。間隙率は両試料間でほとんど差は無いものの、ナノ～マイクロメートルオーダーの間隙径をもつ間隙容量には明瞭な差が見られた。また、本研究における水－岩石反応実験はバッチ法に基づくものであるが、Sr に関する実験結果は初期溶液濃度よりも最終溶液濃度が高く、固相からの溶解（自然溶解）の寄与を考慮する必要があることが指摘された。収着分配係数に関する従来の実験研究では、このような高い自然溶解濃度を考慮することなく溶解核種収着デ

ータが提示されたものが殆どであり、今後、更なる検討を要する。一方、Csについては、ごく僅かの自然溶解しか見られず、少なくとも本材料（多孔質性の軽石混じり凝灰岩）においては、未風化部と風化部との差はほとんど見られなかった。低濃度（ $10^{-6} \sim 10^{-7}$ mol/L）の場合でも、自然溶解の影響よりはイオン強度の方が収着依存性を左右することが観察された。また、初期濃度 10^{-4} mol/L 程度が閾値（飽和濃度）となる可能性が指摘された。

第6章では、未風化部と風化部における間隙特性の相違の観点からの検討が為された。粉末試料とほぼ同重量の立方体の軽石凝灰岩の試料を用いて、同様のバッチ法による水-岩石反応実験を行い、粉末試料を用いた実験結果と比較したものである。立方体試料を用いることで、平均間隙径と全細孔面積の影響に関する知見が得られた。すなわち、平均間隙径は風化部よりも未風化部で大きく、全細孔面積は未風化部の方が風化部よりも増加しており、微細間隙の体積の違いが主な要因であることが示唆された。また、細孔面積を用いて吸着サイトを考慮すると、固相ごく表層の吸着サイトに核種が吸着され実験後に減少するという検討結果となり、二次鉱物の生成に伴う表面積の増加は極めて小さいと結論付けた。

第7章では、本研究から得られた成果と結論をまとめ、今後の研究動向と課題を展望した。

以上のように、本研究は、セシウムおよびストロンチウムの軽石凝灰岩に対する収着能および収着機構に関して、元素による収脱着挙動の違いや岩石の風化変質状態・間隙特性の差異について詳細で系統的な実験および考察を行い、放射性廃棄物処分の核種移行安全評価における新たな知見を与えた。これらの成果は、国際学術雑誌に2編（Geochemical Journal: IF 1.51; Journal of Geoscience and Environmental Protection: IF 0.38）および査読付き国内誌（Transactions, Japanese Geomorphological Union）に英文1編として既に公表されており、超長期にわたる処分場環境の変遷が及ぼす核種移行への影響について、重要な示唆を提起するものである。また、査読中の投稿論文が1編（Journal Radioanalytical and Nuclear Chemistry: IF 1.034）、国際会議（Goldschmidt, EGU）での発表や国内で開催された連合大会（JpGU）の国際セッションでの発表も6件にのぼる。当審査委員会では、これらを総合的に考慮し、博士（学術）の学位に相応しいものであると認め、合格と判定した。