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D5.3 – Second Year Synthesis

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANAGEMENT SKIN

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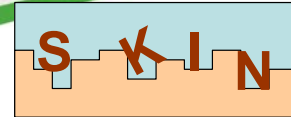
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1. Introduction

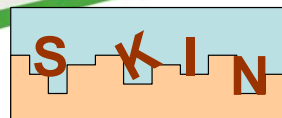
The safety evaluations of all national programmes for the disposal of high level radioactive waste are based on geophysical, hydrogeological and geochemical assessments of processes which may affect the performance of the barrier system for hundreds of thousands of years. Radionuclide retention by adsorption on mineral and engineered barrier material surfaces as well as solubility constraints are always identified as having key safety functions. Solid/liquid chemical equilibrium hypotheses (sorption, solubility, solid-solution formation) are key concepts in the assessment of nuclear waste safety and are always described by local equilibrium hypotheses which are described below.

- In the case of solubility equilibrium of a pure solid phase with an aqueous solution, a maximum solution concentration can be identified. If the flux of radionuclides from dissolving the waste matrices is higher than this maximum threshold solubility value, precipitation is expected to occur. Lists of solubility values of key radionuclides exist in most safety analyses. Ideally, the most stable solid should limit solubility, but less stable metastable phases are often used instead.
- In the case of control of solution concentrations of radionuclides by solid solution formation, equilibrium solution concentrations are expected to be lower than in the case of pure phases. Ra concentrations in equilibrium with pure RaSO_4 are, for example, in the range of 10^{-7} M in natural waters, but in the presence of BaSO_4 solid solutions can form which reduce maximum Ra concentrations by many orders of magnitude. Solid solution control is often ignored in safety analyses for reasons of conservatism.
- In the case of sorption, equilibrium distribution coefficients (K_d) are used, linking the solution concentrations of radionuclides to the concentration of the same radionuclide on the solid phase. The solid/liquid phase boundary is typically considered to be in equilibrium both with the solid and the solution. It is often strongly hydrated and electrically charged, either by the permanent charges on the solid in the near surface region of the solid (e.g. in the case of clays), or by charge build-up due to ionisation of surface sites by interaction with the solvent (“acid/base properties” of the surface), or by specific sorption of charge determining ionic solution species. This leads to the formation of mono- di- or tri-fold innersphere coordinated surface sorption complexes, or to outersphere complex formation, to the establishment of electrochemical



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potential gradients across the interface, and to the build up of an electrical double layer in the adjacent solution, counterbalancing the surface charge.

For radionuclides at trace concentrations this corresponds to constant solution concentrations, or solid/liquid distribution ratios, if environmental conditions remain constant. However, these concepts do not account for irreversible incorporation of radionuclides in the solid phases. Indeed, there is often a gradual and very slow transition from simple adsorption processes to incorporation of trace elements in the surface structure of solid phases. For certain tetravalent actinides apparent solubility equilibrium applies to only the surface without bulk phase equilibrium. This can lead to very large uncertainty in solubility values and derived thermodynamic constants. Equilibrium concepts are characterized by a dynamic state of equal forward/backward reaction rates, under conditions where phase compositions remain constant. Most of the problems arise from a lack of understanding of the dynamics of slow processes close to equilibrium, specifically in the coupling of sorption with other surface equilibrium reactions such as dissolution/precipitation, recrystallisation, isotopic exchange and with the bulk phase equilibrium.

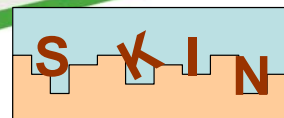
The project SKIN aims to study slow processes influencing radionuclide mobility in close-to-equilibrium conditions in a detailed and systematic manner in relation to surface properties, surface site detachment/attachment kinetics, irreversible sorption and surface incorporation, for cases relevant to the assessment of radionuclide mobility (Ra, Tc, U, Sr, Se...) in nuclear waste repository sites. The development of a method using adsorption from isotopically spiked solution at equilibrium to assess reversibility of solubility equilibria and to understand the mechanism controlling the equilibrium is important in this project. Models are developed to describe this behaviour.

The document presents the advanced research on the questions raised in this project in the mechanism of the coupling between sorption with other surface equilibrium reactions (recrystallisation, isotopic exchange...) and with the bulk phase equilibrium. All the experimental details are reported in the scientific and technical contributions in the 2nd annual workshop (deliverable D6.11).



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2. Methodology

For the long time disposal, individual very slow processes of phases in equilibrium with solution were studied in systematic manner. The processes studied are mainly recrystallization of Barite in the presence of Radium, interaction between Uranium and Iron (III) oxides, isotopic exchange $^{229/232}\text{Th}$ of ThO_2 , entrapment of Se in Calcite, diffusion and advection of ^{90}Sr and ^{45}Ca in cement. To integrate experimental results for modelling, generalized approach suitable for implementation in geochemical modelling codes has been developed based on existing models of time-dependent trace element uptake in host minerals.

An effort has been also done to associate experiments with modelling. As an example, in 2011 and 2012, several meetings were held in Karlsruhe (October 2011), Barcelona (November 2011) and Gothenburg (April 2012) to coordinate the experimental conditions for Ra-uptake and discuss first results (milestone M2.1). These meetings were the occasion to interpret experimental data on barite recrystallization kinetics and on the uptake of radium in the barite structure.

3. Synthesis

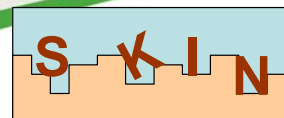
3.1 Solid solution by recrystallisation

If a solid solution is formed by co-precipitation from an aqueous solution containing two radionuclides, the concept of solid solution/aqueous solution thermodynamics is straightforward to apply, even though non-ideality and kinetic effects far-from equilibrium may complicate the picture. The situation is much more difficult if a material such as BaSO_4 exists already as solid in the migration environment, and if a radionuclide such as Ra dissolved from the waste comes into contact with this solid. During the evolution of a nuclear waste repository Ba (mainly ^{134}Ba , ^{135}Ba and ^{138}Ba) may be released during spent fuel corrosion, while UO_2 is precipitated. Together with sulfate in the groundwater, these stable Ba isotopes may form barite (BaSO_4). Moreover, ^{226}Ra forms within the decay chain of ^{238}U , which may be released at a later stage. Thus, Ra may be introduced into a system of barite in equilibrium with Ba and SO_4 . In this case there will be exchange occurring at the surface, but it is less clear whether there will be neoformation of a solid solution with Ra replacing Ba, accompanied by dissolution of the pure BaSO_4 phase (recrystallisation) or whether there will be exchange only in surface regions, and, if so, to what depth?



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Radium uptake during co-precipitation with BaSO_4 is well known (e.g. (Doerner and Hoskins, 1925)). Structure and thermodynamic stability (solubility products etc.) of endmembers BaSO_4 and RaSO_4 are well characterized. Co-precipitation of a $\text{Ba}_x\text{Ra}_{1-x}\text{SO}_4$ binary solid solution from supersaturated solutions has been studied in detail. From the literature, available data suggest almost ideal mixing behavior. Solubility of Ra in equilibrium with $\text{Ba}_x\text{Ra}_{1-x}\text{SO}_4$ solid solutions can be predicted reliably on the basis of available thermodynamic data. The calculated solubility of Ra in equilibrium with $\text{Ba}_x\text{Ra}_{1-x}\text{SO}_4$ solid solutions is several orders of magnitude lower compared to Ra in equilibrium with the pure RaSO_4 endmember.

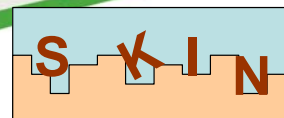
Radium uptake experiments, thermodynamic calculations, structural analysis of the RaSO_4 endmember and complementary co-precipitation experiments were carried out to gain a deeper understanding of the Ra - BaSO_4 exchange process. A special focus of the Ra uptake experiments is the incorporation of radium into barite, the radio-barite recrystallization mechanism, the solid-solution composition and the ^{226}Ra uptake rate as function of environmental conditions. Barite suspensions were equilibrated within a period of up to one year and the barite crystals then characterized by XRD, SEM, and BET. Recrystallization experiments were carried out for two different types of barite with varying surface area Sachtleben ($0.17 \text{ m}^2/\text{g}$) and Aldrich ($1.7 \text{ m}^2/\text{g}$) and an initial Ra concentration of 5×10^{-6} moles/L. Especially for the Sachtleben barite the results indicate a strong recrystallization of the initial barite during the pre-equilibration period, likely not finalized within the equilibration period. After 1-5 months, the pre-equilibrated suspensions were doped with ^{133}Ba and ^{226}Ra . For the combined ^{133}Ba ^{226}Ra experiments, monitoring of the aqueous ^{133}Ba and ^{226}Ra concentrations is ongoing whereas first results from the ^{226}Ra barite recrystallization experiments at room temperature and at $90 \text{ }^\circ\text{C}$ are presented below for two different types of barite, Sachtleben ($0.17 \text{ m}^2/\text{g}$) and Aldrich ($1.7 \text{ m}^2/\text{g}$).

The experimental results show a decrease to a plateau of the Ra concentration of 3×10^{-9} to 7×10^{-9} mol/L within the first 70 days of the experiment at a solid/liquid ratio of 5 g/L . At a solid/liquid ratio of 0.5 g/L a slower decrease of the Ra concentration is observed to a plateau of about 2×10^{-8} mol/L after 180 days for the barite with the lower surface area (Sachtleben) whereas the barite with the higher surface area reaches similar concentrations of about 4×10^{-8} mol/L after more than 350 days. The decrease of the Ra concentration is apparently not related to the specific surface area of the barite powders. A slightly higher and faster Ra uptake is consistently observed for the barite type with lower surface area. Barium concentrations are slightly above the calculated solubility in all experiments. First results of TOF-SIMS analyses using the Sachtleben barite after



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350 days from the recrystallization experiments at ambient conditions with 0.5 and 5 g/L indicate the uptake of Ra into the crystal volume.

At 90 °C Radium uptake into barite during batch recrystallization experiments is significantly lower than at room temperature. Ba concentrations indicate near to equilibrium conditions with respect to the barite end-member after ~ 1 day. Compared to room temperature, faster uptake kinetics for Ra are observed at 90 °C. The steady state of the Ra concentration is reached at 3×10^{-8} mol/L for experiments at 90°C and at 3.5×10^{-9} mol/l for experiments at room temperature, corresponding well with the endmember solubilities at room temperature and 90 °C. At room temperature, RaSO_4 is less soluble than BaSO_4 whereas solubilities estimated with GEMS-PSI using the Nagra-PSI database indicate that RaSO_4 is more soluble than barite at 90 °C. As a consequence, a lower uptake of Ra can be expected for 90 °C.

In addition, EXAFS and X-ray powder diffraction was performed to gain detailed structural information about the RaSO_4 end-member. The unit cell parameters of radium sulphate were determined to be orthorhombic, belonging to the Pnma (No. 62) space group with the cell parameters $a = 9.07 \text{ \AA}$, $b = 5.52 \text{ \AA}$, $c = 7.28 \text{ \AA}$ and $V = 364.48 \text{ \AA}^3$. These data support the fact that radium sulphate is isostructural with barium-, strontium- and lead sulphate. The mean Ra-O and S-O bond distances determined using EXAFS were found to be $2.96(2) \text{ \AA}$ and $1.485(8) \text{ \AA}$ respectively and the Ra-O-S bond angle was $127(2)^\circ$. These data were consistent with and supported by the XRD data. These findings indicate that it is possible for radium to co-precipitate with barium, strontium and lead in sulphate media to form a substitution solid solution.

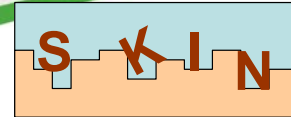
From the experimental values, the data were fitted using the following two-step procedure and evaluation the deviation from the ideality for ideal solid solutions and non-ideal solid solutions with non-ideality parameters set to $a_0 = 1.0$ and $a_0 = -0.8$, respectively:

- (a) Calculation with the GEM-Selektor (GEMS) code of a series of equilibrium states as a function of the increasing amount (n) of $(\text{Ra},\text{Ba})\text{SO}_4$. This yields the equilibrium Ra concentrations as a function of n up to the total amount of barite used in the experiments and for the selected solid solution model (ideal or non-ideal).
- (b) Determination of the reaction time t as a function of n , the initial specific surface area σ (m^2/g), the solution volume V (L), the particle concentration S/L (g/L) and a recrystallization rate R ($\text{mol m}^{-2} \text{ d}^{-1}$) normalized to the initial mineral surface:



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$$t = \frac{n}{\sigma V(S/L)R}$$

For each value of n calculated with GEMS, a reaction time can be determined from the equation above. Because the GEMS calculations include the concentrations of Ra at equilibrium with the selected solid solution, each $t(n)$ value can be readily associated to the corresponding equilibrium Ra concentration, $[Ra](n)$. Since there is no independent determination of the recrystallization rate in these experiments, R was used as adjustable parameter to fit the Ra concentration data.

The modelling results point to formation of an ideal solid solution (Aldrich) or even a non-ideal solid solution with negative enthalpy of mixing (Sachtleben). This latter result is not consistent with the findings of earlier experiments described by (Bosbach et al., 2010; Curti et al., 2010) who indicate (Ra,Ba)SO₄ solid solutions with positive Guggenheim parameters.

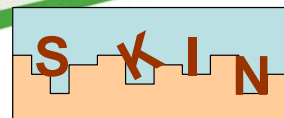
The extrapolation to zero ionic strength of the original data (at 20 °C), yields a somewhat lower solubility product and is statistically less accurate than the values given by (Nikitin and Tomatscheff, 1933) (-10.37 ± 0.02) obtained using the activity coefficients tabulated by (Lewis and Randall, 1927). These authors give a generic value (applying to all divalent cations) for the activity coefficient of Ra²⁺. Although it is quite surprising that Lewis and Randall's method performs better than more modern methods of ionic strength corrections, one has to acknowledge this as a fact. However, both methods yield almost equivalent results for the value of the RaSO₄ solubility product, and we see no need for a modification of the value used so far ($\log K_{sp}^0 = -10.26$). This result reasonably agrees with the evaluation of the same data made by (Paige et al., 1998), who obtained $\log K_{sp}^0(25 \text{ }^\circ\text{C}) = -10.21 \pm 0.06$ using the Pitzer model.

Taking into account the new evaluations, one can now assign an uncertainty range of $\pm 0.1 \log K$ units to the solubility product of RaSO₄. Using the temperature dependence equation of (Langmuir and Riese, 1985) one then derives $\log K_{sp}^0 = -10.4 \pm 0.1$ for experiments carried out in a laboratory environment thermostated at 20 °C. This puts a lower solubility limit at $\log K_{sp}^0 = -10.5$ for the experiments carried out at FZJ, which could help explaining the low Ra concentrations found in some experiments (leading to negative interaction coefficients when using $\log K_{sp}^0 = -10.26$).



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3.2 Retention, co-precipitation and rearrangement processes

Most of the primary solids, as well as the secondary solid phases expected to form under repository conditions after the eventual release of the radionuclides present in the different waste forms are oxides which, in a first stage, will be of a rather amorphous nature, thus having hydrous surfaces. In principle these solids are only sparingly soluble, so that apparent equilibrium states are reached in relatively short time periods. Nevertheless, the amorphous nature of these surfaces enhances the dynamism of the systems, so that they are not under real equilibrium, but in a continuous evolution. The influence of iron(III) oxides has been also considered as a relevant retardation factor for radionuclide migration, although the evolution of this interaction with time, as the solid phase ages, has not been sufficiently addressed in previous investigations. The rearrangement of the initially open structure may cause release of the radionuclides initially trapped in the amorphous structure of the corrosion product. Such structural re-ordering is a slow process that has not been tackled with in combination with the implications for retention of minor components. The study will link sorption with stronger co-precipitation reactions to assess the fate of the minor incorporated components in the long-term. This research needs of the use of focused analytical techniques allowing the investigating the evolution of the surfaces.

Iron oxides are the main products of canister corrosion and can be present among the engineered and geological barriers. Among the iron oxides, the amorphous ferrihydrite is one of the most widespread iron solids and an important precursor of more stable and crystalline iron oxides. Ferrihydrite evolution with time and the final products formed depend on many factors, such as pH, time, temperature, etc. The presence of foreign species (such as uranium) in the system will affect the ferrihydrite ageing process. The ageing and transformation process of ferrihydrite will affect in turn the solubility and the retention/release process of uranium from the co-precipitates.

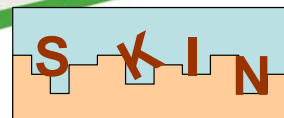
According to the XRD analysis of the samples aged at 3 weeks and 9 years, the bulk of U(VI)-Fe(III) co-precipitates can be assumed to evolve from a 2L ferrihydrite to a 6L ferrihydrite-like. The results obtained in the EXAFS (Fe K-edge) measurements were consistent with the XRD results. The results obtained in the EXAFS (U L_{III}-edge) measurements are consistent with an edge-sharing bond between U(VI) and ferrihydrite. Those results also indicate that the bonding environment of uranium in the co-precipitates evolves with ageing time, towards a schoepite-like structure.

The preliminary conclusion obtained from that observations indicate that the retention of U(VI) within the ferrihydrite structure remains effective after 5 weeks of suspension



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and after 11 years of a dry-stored sample. Uranium is affected by the ageing process, and the results indicate a re-arranging of the uranium content towards a schoepite-like structure. This would suggest that the assessment of the efficiency of this retention process at long time frames could be governed by the schoepite solubility limit.

3.3 Solubility

The solubility concept, even if fundamental in safety analyses, is not always simple to apply. For example, if the solubility controlling phase is already present in the solid/water system, and if the radioisotope is initially not part of the solubility controlling solid. Solubility equilibrium always involves exchange at the surface, but recently it has been shown that in certain cases, such as tetravalent actinides, equilibrium with the bulk phase may not be attained due to very slow surface dissolution rates. Moreover, in many cases reversibility is not certain, since a supposed equilibrium state attained for example from undersaturated conditions cannot be validated by approaching it from oversaturated conditions because solids formed under these conditions often differ from those used in undersaturated conditions. Here again slow surface reaction kinetics is at the origin of the problems.

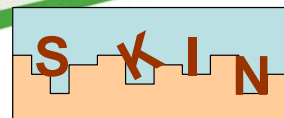
Solubility data are also used to constrain thermodynamic models, for example the Gibbs free energy of free Zr^{4+} ions in solution was determined from solubility data. Thermodynamic models are used in advanced safety analyses to describe the solubility response to varying geochemical conditions. Thermodynamic models, however, can only be applied if reversibility by equal surface atom detachment and attachment probabilities is certain. According to affinity-based solid dissolution models, forward reaction rates far from-equilibrium should be similar to those close to equilibrium, only the net-dissolution rate decreases due to the back reaction. The situation is more complicated with slow reactions such as the dissolution rate of ThO_2 for which the detachment of a monolayer may take up to 300 years. Surfaces of a certain roughness will initially have a number of atoms at defect sites, edges, corners, high energy sites, grain boundary materials etc., and the detachment rate of these atoms will govern the apparent dissolution rate. Hence the forward dissolution rate is not necessary constant as assumed in the affinity theory of solid dissolution and solubility, but it depends on time, and apparent equilibrium may involve certain surface sites (attachment/detachment) without involving the whole surface. These problems may also be important for UO_2 (spent fuel) dissolution under reducing close-to-equilibrium conditions.

Solubility measurements indicate that the oxide surfaces do not behave in the same way as the bulk solid. A specific experimental programme is set up to investigate the effect



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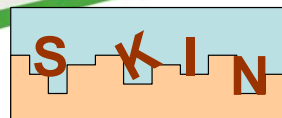
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of the surfaces on the measured solubilities. Previous studies on dissolution of $\text{ThO}_2(\text{c})$ indicate that the dissolution is very dependent on the material at the grain boundary. 80 % of the XPS accessible near surface region of sintered thorium oxide is represented by the less reactive $\text{ThO}_2(\text{cr})$ grains. The remaining 20 % corresponds to $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$ which is largely associated with grain boundaries. The empirical solubility data does not correspond to thermodynamic bulk phase/solution equilibrium, as measured solution concentrations are controlled by specific site exchange mechanisms at the solid/solution interface. Therefore for sparingly soluble solids, one needs to quantify the specific surface site involved in the attachment and detachment rates if one wants to assess solubility constraints.

Different crystalline states of thorium oxide surfaces without the grain boundaries were synthesized and studied in this work and compared with crushed and washed HTR sphere of ThO_2 . Four sets of were studied: (i) Crushed ThO_2 spheres, (ii) Initial ThO_2 spheres, (iii) ThO_2 powder synthesized at 1300°C and (iv) ThO_2 powder synthesized at 700°C . After about 50 days, the pseudo steady-state equilibrium is reached for all samples. The concentration of Th for the powder synthesized at 1300°C and the crushed sphere are close (2.98×10^{-8} mol/L and 2.95×10^{-8} mol/L, respectively). It seems that the global and the kinetic dissolution behaviours are similar for these two samples. The crystalline state of the samples is involved in the dissolution mechanism during the initial kinetic dissolution and the reaching of the pseudo steady-state equilibrium. The ratio between grain and grains boundaries and the global and kinetic dissolution behaviour can be described as following: ThO_2 powder synthesized at 700°C > Initial ThO_2 spheres > Crushed ThO_2 spheres = ThO_2 powder synthesized at 1300°C .

The different behaviour of the surfaces of ThO_2 versus the surface crystalline state has been described. The use of the isotopic $^{229}\text{Th}/^{232}\text{Th}$ exchange assesses the key issue on the question of solubility: the realistic solubility behaviour of the ThO_2 surface. The 4 sets of solid samples versus the leaching behavior have been classified: (IV) > (II) > (I) = (III) with (I) Crushed ThO_2 spheres, (II) Initial ThO_2 spheres, (III) ThO_2 powder synthesized at 1300°C , (IV) ThO_2 powder synthesized at 700°C . Moreover, the behavior of the solid versus the $^{229}\text{Th}/^{232}\text{Th}$ exchange occurs if the $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$ phase is implied into the solid surface leaching.



4. Conclusion

Key concepts describing maximum solution concentrations and retention behaviour of radionuclides in the assessment of nuclear waste safety by local or global solid/liquid chemical equilibrium hypotheses (sorption, solubility, solid-solution formation) were assessed by evaluating the effect of surface properties on apparent solubility as well as the kinetics of incorporation of radionuclides in the structure of a solid phase. The equilibrium concepts characterized by a dynamic state of equal forward/backward reaction rates were here described for the three main hypotheses: solubility equilibrium of a pure solid phase with an aqueous solution (eg. ThO_2), control of solution concentrations of radionuclides by solid solution formation (eg. Ra-BaSO_4) and sorption/retention (eg. U(VI)-Ferrhydrite). The understanding on the mechanisms controlling the local equilibrium and the very slow processes in conditions close to equilibrium were reached for various solids in a systematic manner by using isotope exchange under close-to-equilibrium conditions. The use of isotope as a chemical analogue of the element probed in the conditions close-to-equilibrium has allowed to explain the mechanisms controlling the reaction in those conditions (eg. formation of a solid solution of $\text{Ba}_x\text{Ra}_{1-x}\text{SO}_4$ by recrystallisation) and to give an accurate solubility value compare to the available data in literature.

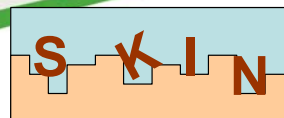
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