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Nitric Acid Adducts Formation During Crystallization of Barium and Strontium Nitrates and their Co-precipitation from Nitric Acid Media

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$Ba(NO_3)_2$ precipitation is one of the limiting factors in HLW evaporation during NPP spent fuel reprocessing. The model was proposed in our previous work [1] for approximation of the $Ba(NO_3)_2$ and $Sr(NO_3)_2$ solubility in HNO_3 solutions using the law of mass action. As a result the two linear areas were identified according to slope of the solubility on total nitrate ion concentration in logarithmic scale and the existence of the adducts, containing 1-2 molecules HNO_3 molecules with $Ba(NO_3)_2$ and 2 ones with $Sr(NO_3)_2$ were suggested. The $Ba(NO_3)_2$ solubility in neutral solutions of $Sr(NO_3)_2$ is higher, while in the presence of ammonium and sodium or RE nitrates the curve shape is also characterized by the minimum, indicating in all the cases on the effect of nitrate complexation. In $Ba(NO_3)_2$ KNO_3 system the formation of the slightly soluble double salt $Ba(NO_3)_2 \cdot 2KNO_3$ is observed.

The chemical analysis using ^{137}Cs or $Be(NO_3)_2$ as a reference mark in the case of $Ba(NO_3)_2$ or $Sr(NO_3)_2$, respectively, was carried out to calculate the volume of mother liquor captured by the precipitate. The amount of excess NO_3^- ion was compared with the excess of H^+ ion in relation to metal amount in the precipitate. $Ba(NO_3)_2$ and $Sr(NO_3)_2$ precipitates in the range from 0 to 5 mol/dm³ HNO_3 contained only small permanent amount of excess, occluded by precipitate. Increasing of HNO_3 concentration in the liquor > 7 mol/dm³ HNO_3 led to a sharp increase of acid content in precipitates, indicating on the complex compound formation during crystallization. In the same area co-crystallization of Ba and Sr nitrates took place.

IR spectra [2] including differential ones confirm the presence of excess nitric acid and/or water in wet precipitates of barium and strontium nitrates and in their solid solutions precipitated at the high acidity or obtained by re-crystallization during their mixing in wet form.

X-ray diffraction patterns and chemical analysis [2] of individual and co-crystallized barium and strontium nitrates also indicated on the formation of $(Ba,Sr)(NO_3)_2$ solid solutions of three compositions at 4 mol/dm³ HNO_3 and more in mother liquor, the composition depending on Sr to Ba ratio in the liquor at significant $Sr(NO_3)_2$ molar excess and typical solubility of the latter. The pattern of double salt $Ba(NO_3)_2 \cdot 2KNO_3$ was identified as well.

So, the formation of adducts of barium and strontium nitrates with nitric acid was qualitatively confirmed by different methods indicating on their metastable nature, resulting in possible displacement of nitric acid monohydrate from forming matrix into pores of crystals.

1. Mishina, N.E., Akhmatov, A.A., Zilberman, B.Ya., et al. Radiochemistry, 2010, vol. 52, Iss. 5, pp 523-529.

2. Mishina, N.E., Zilberman, B.Ya., Lumpov, A.A., et al. Radiochemistry, 2013, vol. 55, Iss. 2, pp (in printing).

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