

Letter to the Editor

# Comparison of binding energy to the sorption enthalpy of radionuclides with trap materials used in LMFBRs

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## Abstract

In liquid metal fast breeder reactors (LMFBR), traps are provided in the primary coolant circuit to reduce the contamination due to the deposition of long lived  $\gamma$ -emitting nuclides. The binding energies of the radionuclides with iron and nickel were estimated using Pauling's electronegativity. The results are comparable to the sorption enthalpies derived from the experimental isotherms.

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## 1. Introduction

In the course of operation of LMFBR, trace amounts of radionuclides get released into the coolant, and are transported and deposited along the walls of the primary piping system components [1]. This becomes a significant source of radiation exposure while carrying out maintenance work on these components. Control measures need to be instituted to keep the concentration of radionuclides in the coolant and hence the deposited activity on the wetting surfaces to remain at a lower level.

Past experience with LMFBRs shows that the predominant radionuclides fall into three different categories.

- (i) The activation products of the liquid sodium is used as coolant ( $^{22}\text{Na}$  and  $^{24}\text{Na}$ ). While this source of contamination is inevitable, the exposure from it can be appreciably reduced by taking

up maintenance work after a waiting period of about a week after shut down, which allows the major radionuclide  $^{24}\text{Na}$  (half life 15 h) to decay.

- (ii) Corrosion products like  $^{54}\text{Mn}$  and  $^{60}\text{Co}$  resulting from the activation of structural materials through the reactions  $^{54}\text{Fe}(n,p)^{54}\text{Mn}$ ,  $^{60}\text{Ni}(n,p)^{60}\text{Co}$ , respectively. In the absence of fission products referred in the sequel, these constitute the prime sources of contamination.
- (iii) Fission products like  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$  and  $^{131}\text{I}$  released from failed fuel pins. These may not be present always. But practicality dictates that reactor be permitted to operate even with a few failed pins if needed, making them potential sources. Operating experience of Russian fast reactor BN-600 has shown the deposition of  $^{137}\text{Cs}$  [2]. Because of its volatile nature, this nuclide was observed to deposit preferentially in the low temperature cover gas space thus forcing a complicated maintenance schedule.

Although radiologically very significant, these nuclides are present in the coolant with very low mass

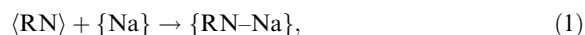
*E-mail address:* [kss@igcar.ernet.in](mailto:kss@igcar.ernet.in)

concentration. This rules out their reduction by solid phase separation and precipitation. Hence, use of materials that can act as radionuclide trap (RNT) is recommended to achieve this reduction. The provision of such traps in the coolant circuit has been reported in several operating reactors [1]. Mc Guire and Brehm [3] used nickel foils above the core as traps for  $^{54}\text{Mn}$ . Stamm et al. [5] tested different materials in the German reactor, KNK-II and observed that nickel pall rings sorbed about 110 times the amount of  $^{54}\text{Mn}$  compared to the stainless steel pall rings. With respect to cesium, Krasnoyanov et al. [4] carried out experiments involving graphite as trapping material. In the Russian reactor BOR-60, use of such trap for 45 h reduced the activity due to cesium by a factor of 4 and the  $\gamma$ -dose by 2.6. Similarly, in another reactor BN-350, the dose rate was reduced by a factor of 1.5–2.0 in the first campaign and by a factor of 1.7 in the subsequent campaign. On the other hand, in the reactor BN-600 use of reticulated vitreous carbon (RVC) was recommended as the material for cesium [2]. Muralidaran et al. [6,7] designed and developed a trap for cesium using RVC to be used in fast breeder test reactor (FBTR), India.

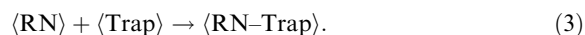
No single trapping material is efficient for all the nuclides, obviously due to the differences in their chemical properties. Selecting the best material for each radionuclide forms an important task. This is usually done based on experimental investigations which are time consuming. It would be helpful to narrow down the choices based on empirical estimates of binding energy for trapping. This note examines the usefulness of one of the earlier methods of estimating the reaction energy [8] based on Pauling's electronegativity for this purpose. The method is applied to several test cases and the estimated energies compared with sorption enthalpies based on measured sorption isotherms.

## 2. Methodology

Consider the reaction between the radionuclide (RN) and the trap material



Adding (1) and (2), we get



Thus the energy involved in (3) represents the sorption enthalpy. This value can be estimated using the Pauling's electronegativity and binding energy of the radionuclide with the trap material that is described below.

### 2.1. Binding energy from the electronegativity and sublimation enthalpy

According to Linus Pauling [9] the enthalpy of formation of a substance is proportional to the square of the electronegativity difference between the two atoms. This concept of electronegativity is slightly modified as follows to address the practical problem under consideration.

$$D_{(A-B)} = \{ D_{(A-A)} D_{(B-B)} \}^{1/2} + 96.5 \Delta\chi^2, \quad (4)$$

where  $D_{(A-B)}$  is the binding energy between trap material and radionuclide ( $\text{kJ mol}^{-1}$ );  $D_{(A-A)}$ , Binding energy between radionuclide atoms ( $\text{kJ mol}^{-1}$ );  $D_{(B-B)}$ , Binding energy between trap material atoms ( $\text{kJ mol}^{-1}$ ). And  $\Delta\chi$  = the difference in the electronegativity between the trap and the radionuclide atoms.

Thus the calculation of  $D_{A-B}$  requires data on  $D_{A-A}$ , and  $D_{B-B}$ , and electronegativity of A and B.  $D_{A-A}$  or  $D_{B-B}$  is calculated by the following relation:

$$= (n/N) \Delta H_{\text{vap}}. \quad (5)$$

$N$  and  $n$  represent the coordination number of the element and number of atoms contributing to one bond in the crystal, respectively. The input values are taken from Emsley [10].

## 3. Results and discussions

The stated methodology was applied for the estimation of binding energies of RNT, iron and nickel, for radionuclides  $^{60}\text{Co}$ ,  $^{54}\text{Mn}$  and  $^{137}\text{Cs}$ . The calculation was also extended to binding of mercury on copper. A comparison of the estimated binding energies with the sorption enthalpies derived from isotherms reported in literature is presented in Table 1.

Measured sorption isotherms involving the sodium system are generally scarce. The data for manganese and cobalt on nickel and iron were derived from the isotherms of Bobkov et al. [2]. The investigation on sorption of manganese and cobalt includes polished nickel, iron, stainless steel and iron–manganese alloy in the temperature range 200–400 °C. The sorption isotherms for cesium with materials like nickel, stainless steel, oxidised zirconium and single crystal  $\text{Al}_2\text{O}_3$  have been reported by Cooper and Taylor [12]. The isotherms were measured at 150 °C, 260 °C, 480 °C and 535 °C over cesium concentrations from 0.03 at. ppm to 46 at. ppm. Nickel and  $\text{Al}_2\text{O}_3$  were noted to be superior materials for trapping cesium. The sorption enthalpy for binding of mercury on copper was obtained from Ref. [7].

It can be seen that the enthalpies of sorption of manganese on nickel and iron compare favourably with the corresponding binding energies. The agreement is even better in the case of mercury sorption on copper.

Table 1  
Comparison of binding energy and sorption enthalpy

Radionuclide	Trap element	Binding energy (kJmol <sup>-1</sup> )	Sorption enthalpy (kJmol <sup>-1</sup> )	Reference
Mn	Fe	79.37	62.114	[9]
	Ni	67.042	60.6887	
Co	Fe	76.11	21.1907	
	Ni	62.85	15.730	
Cs	Ni	150.0	30.0	[11]
Hg <sup>a</sup>	Cu	44.70	45.35	[7]

<sup>a</sup> Note: The coordination number for mercury used in Eq. (5) was taken from [13].

In the case of cobalt, the binding energies with nickel and iron differ considerably from their respective sorption enthalpies. Nevertheless, the sorption enthalpy values are less than the enthalpy of solution of cobalt in sodium (28.0 kJmol<sup>-1</sup>) [11]. Further, Bobkov et al. [2] reported that the adsorption of cobalt on to these metals were of activated chemisorption type. It is well known that the energy associated with this type of adsorption is greater than 50 kJmol<sup>-1</sup>. In view of these observations, the experimental sorption enthalpies of cobalt on nickel and iron need further investigation.

The sorption enthalpy of cesium on nickel derived from the experimental isotherms of Cooper and Taylor [12] is 28 kJmol<sup>-1</sup>. In this case again, the comparison is not satisfactory with the estimated binding energy being higher by a factor of about five compared to the derived sorption enthalpy. This can be attributed to the large electronegativity difference leading to the ionic bond between cesium and nickel. Moreover, Cooper and Taylor [12] mentioned that the oxygen concentration in sodium during the measurements was about 30 ppm, which had resulted in the deposition of cesium in the form of Cs<sub>2</sub>O rather than in its elemental form. It was further observed that cesium formed multi-layers with nickel possibly resulting in the observed lower value for sorption enthalpy. This case illustrates the possible limitation of the proposed method when applied to complex trapping processes.

To summarise, the binding energies of the radionuclides with trap materials iron, nickel and copper have been estimated. These values are shown to be in good agreement with the sorption enthalpies obtained from the experimental isotherms, particularly for elemental trapping process. In view of this, the proposed method of binding energy estimate may serve as an additional tool for the selection of trap material.

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#### References

- [1] H. Feuerstein, A.J. Hooper, F.A. Johnson, *At. Energ. Rev.* 17 (3) (1979) 697.
- [2] Yu.G. Bobkov et al., Meeting on Fission and Corrosion Product Behaviour in Primary Circuits of LMFBRs, Karlsruhe (Germany), 5–8 May 1987, IWGFR-64, p. 51.
- [3] J.C. Mc Guire, W.F. Brehm, *Nucl. Technol.* 48 (1988) 101.
- [4] H. Stamm et al., *Liquid Metal Engineering and Technology*, 9–13 April 1984, Ed. BNES, p. 137.
- [5] Krasnoyanov et al., *Liquid Metal Engineering and Technology*, 9–13 April 1984, Ed. BNES, p. 185.
- [6] P. Muralidaran et al., Nuclear and Radiochemistry Symposium, 21–24 February 1995, p. 258.
- [7] V. Ganesan, P. Muralidaran, K. Chandran, G. Periasamy, National Symposium on Management of Radioactive and Toxic Wastes, 17–19 March 1993, Kalpakkam, p. 84.
- [8] C. Guminski, *Z. Metallkd.* 81 (1990) 105.
- [9] L. Pauling, *Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd Ed., 1969.
- [10] John Emsley, *The Elements*, ELBS edition, 1992.
- [11] Stanaway et al., in: H.U. Boursstedt (Ed.), *Metal Behaviour and Physical Chemistry in Liquid Metal Systems*, Plenum, New York, 1981, p. 421.
- [12] M.H. Cooper, G.R. Taylor, *Nucl. Technol.* 12 (1971) 83.
- [13] T. Ida, R.I.L. Guthrie, *The Physical Properties of Liquid Metals*, Clarendon, Oxford, 1988.