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Gamma Radiolytic Decomposition of KNO_3 in Presence of Aluminium and Its Compounds

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The present work has been carried out to investigate the effect of aluminium and its different compounds on the radiolytic decomposition of potassium nitrate. The radiolytic decomposition of the admixtures has been studied over a range of gamma dose of 1–110 KGy. The amount of nitrite formed was estimated spectrophotometrically. In case of admixtures of aluminium powder and sodium aluminate with potassium nitrate the G values have been found to increase with increase in their mole fractions while in case of admixtures of aluminium oxide and potash alum with potassium nitrate a reverse trend is seen. The increase in G values has been attributed to the transfer of energy absorbed by the additives or *vice-versa.*

Key Words: Gamma radiolysis, Potassium nitrate, Al additives.

INTRODUCTION

The gamma rays being ionizing radiations bring about many visible changes such as fluorescence, colouration in glass, changes in crystallographic structures, destruction of existing species as well as formation of new species[1] etc. The radiolysis of inorganic nitrates has been studied widely[2–4]. Gamma radiations decompose the nitrates to nitrites along with the formation of other radiolytic products. ESR study of γ-irradiated single crystal of $K(UO_2)(NO_3)_3$ by Gundu Rao *et al.*[5] showed the presence of NO_3 radical at room temperature and NO_3^{2+} at 77K. γ-irradiated KNO_3 crystals[14] by EPR[6] showed the presence of NO_2, NO, NO_3^-. The effect of particle size of nitrate as heterophase impurity on radiolysis of pure and Ba^{2+} doped KNO_3 crystals has also been reported[7]. The decomposition mechanism of nitrate as given by Muhammad and Maddock[8] is as follows:

$$2NO_3^- \longrightarrow NO_3 + NO_3^{2-}$$
$$3NO_3^- \longrightarrow NO_3 + NO_2^{2+} + NO_2^- + O_2$$
$$2NO_3^- \longrightarrow 2NO_2^- + O_2$$
$$NO_3^- \longrightarrow NO_3 + e$$

These reactions occur at relatively low temperature but as the temperature approaches room temperature the reaction increasingly becomes

$$2NO_3^- \longrightarrow 2NO_2^- + O_2$$

But the possibility of the formation of paramagnetic radicals cannot be ruled out. There appears to be a general consensus over the formation of paramagnetic radical species such as NO_2, NO_3^{2-} and NO_3 during γ-radiolysis of nitrates. Several other species such as NO_2^{2-}, NO, O^- and O^{2-} have also been identified.

When additives are used in these nitrates, radiolytic decomposition may get accelerated and increase in G value is observed. Some additives may protect the nitrates thereby decreasing the G values. The present paper aims to investigate the effect of aluminium and its different compounds on the radiolytic decomposition of potassium nitrate.

EXPERIMENTAL

All the solutions were prepared in doubly distilled water. The admixtures of potassium nitrate (0.2–0.8 mole fractions) with potash alum, aluminium oxide and aluminium metal powder were prepared by mixing the calculated quantities of these substances. The mixtures were ground in an agate mortar and passed through a sieve of 100 mesh. The freshly prepared mixtures were used for irradiation purpose. Because of hygroscopic nature of sodium aluminate, mole fractions between 0.02 to 0.08 could only be studied. Gamma irradiation was carried out in unsealed corning glass tubes in Cobalt-60 Gamma Chamber 900 (GC 900) at a dose rate of 1.4 KGy g^{-1} h^{-1} (8.74×10^{18} eV g^{-1} h^{-1}) which was measured by Fricke Dosimeter[9]. The amount of nitrite formed was estimated spectrophotometrically by Shinn'a diazotization[10] method by measuring the absorbance at $\lambda_{max} = 540$ nm using ELICO SL-150 and Shimadzu UV-240 spectrophotometer.

RESULTS AND DISCUSSION

Pure KNO_3 and the admixtures of KNO_3 were irradiated for various doses in the range of 2–110 KGy. The $G(NO_2^-)$ values and the amount of nitrite formed per g of the mixture irradiated are given for 0.2 to 0.8 mole fractions of admixtures (0.02–0.08 in case of sodium aluminate) in Tables 1–4. The variation of concentration of nitrite formed and $G(NO_2^-)$ values against absorbed doses, for admixtures of different mole fractions, are shown in Figs. 1 and 2. It is seen that the concentration of nitrite formed increases linearly over the range of dose studied in admixtures of potassium nitrate with potash alum, aluminium oxide and sodium aluminate. It has been observed that the G values and the amount of nitrite formed are quite high in admixtures of aluminium powder and potassium nitrate. For admixture of KNO_3 and Al powder, the G values are 1.153, 18.377, 25.029 and 50.624 at mole fractions 0.2, 0.4, 0.6 and 0.8 respectively at a dose of 1 KGy. As the mole fraction increases, these values are also found to increase. However, with the increase in absorbed dose all of them show a decreasing trend. In case of admixtures of sodium aluminate with potassium nitrate a similar trend has been observed, but the G values are comparatively lower than those in admixture of aluminium powder and potassium nitrate.

VARIATIONS IN CONCENTRATION OF NO_2^- AND $G(NO_2^-)$ IN ACCORDANCE WITH THE DOSE ABSORBED AND MOLE FRACTIONS OF THE VARIOUS ADMIXTURES OF KNO_3 AND Al COMPOUNDS

TABLE-1

Dose (KGy)	Potash alum + KNO_3				Potash alum + KNO_3			
	0.2	0.4	0.6	0.8	0.2	0.4	0.6	0.8
	NO_2^- (ppm)	NO_2^- (ppm)	NO_2^- (ppm)	NO_2^- (ppm)	$G(NO_2^-)$	$G(NO_2^-)$	$G(NO_2^-)$	$G(NO_2^-)$
4	11.13	6.02	3.72	1.73	0.572	0.312	0.195	0.089
5	13.24	6.11	3.24	1.65	0.518	0.256	0.135	0.069
8	20.26	10.06	5.32	3.01	0.529	0.264	0.140	0.078
15	39.11	22.48	7.55	7.01	0.547	0.309	0.106	0.096
47	110.09	55.70	38.86	10.23	0.488	0.249	0.174	0.046
80	115.73	89.79	62.71	20.67	0.409	0.236	0.165	0.054
105	217.36	139.20	57.24	28.25	0.428	0.275	0.113	0.056

TABLE-2

Dose (KGy)	Al oxide + KNO_3				Al oxide + KNO_3			
	0.2	0.4	0.6	0.8	0.2	0.4	0.6	0.8
	NO_2^- (ppm)	NO_2^- (ppm)	NO_2^- (ppm)	NO_2^- (ppm)	$G(NO_2^-)$	$G(NO_2^-)$	$G(NO_2^-)$	$G(NO_2^-)$
1	7.48	14.50	10.86	12.67	1.535	1.804	2.239	2.613
5	28.48	29.08	25.59	30.81	1.202	1.219	1.070	1.289
7	36.93	33.54	54.55	32.52	1.106	0.991	1.612	0.974
15	72.13	75.78	78.50	56.70	1.010	1.059	1.098	0.793
24	106.32	93.94	111.04	70.69	0.915	0.805	0.863	0.606
47	187.28	177.22	130.98	126.37	0.836	0.791	0.585	0.559
105	421.94	367.25	267.78	193.59	0.835	0.727	0.530	0.387

TABLE-3

Dose (KGy)	Sodium aluminate + KNO_3				Sodium aluminate + KNO_3			
	0.02	0.04	0.06	0.08	0.02	0.04	0.06	0.08
	NO_2^- (ppm)	NO_2^- (ppm)	NO_2^- (ppm)	NO_2^- (ppm)	$G(NO_2^-)$	$G(NO_2^-)$	$G(NO_2^-)$	$G(NO_2^-)$
2	38.74	52.82	55.22	62.61	3.987	5.436	5.708	6.547
5	33.92	65.44	69.17	87.75	1.403	2.726	2.893	3.580
8	76.58	78.89	89.79	99.04	1.991	2.056	2.354	2.537
24	117.33	181.37	157.91	180.60	1.027	1.609	1.382	1.562
47	243.71	412.62	252.21	269.60	1.064	1.326	1.121	1.189
80	372.59	298.33	381.10	427.29	0.979	1.096	1.000	1.121
105	466.55	487.65	488.01	535.12	0.928	0.956	0.972	1.059

TABLE-4

Dose (KGy)	Al powder + KNO_3				Al powder + KNO_3			
	0.2	0.4	0.6	0.8	0.2	0.4	0.6	0.8
	NO_2^- (ppm)	NO_2^- (ppm)	NO_2^- (ppm)	NO_2^- (ppm)	$G(NO_2^-)$	$G(NO_2^-)$	$G(NO_2^-)$	$G(NO_2^-)$
1	5.61	88.68	1123.45	257.11	1.153	18.377	25.029	50.624
2	11.55	247.65	139.49	343.91	1.188	25.661	14.243	33.858
8	50.31	974.17	407.63	687.00	1.317	25.520	10.630	17.814
10	48.43	782.00	767.83	592.78	1.017	16.425	16.081	12.451
24	93.18	1094.45	782.66	1720.96	0.806	9.919	6.698	14.974
47	195.89	234.79	2170.64	2259.26	0.865	1.047	9.121	9.928
80	312.70	410.48	1619.32	2440.53	0.821	1.076	4.255	6.482

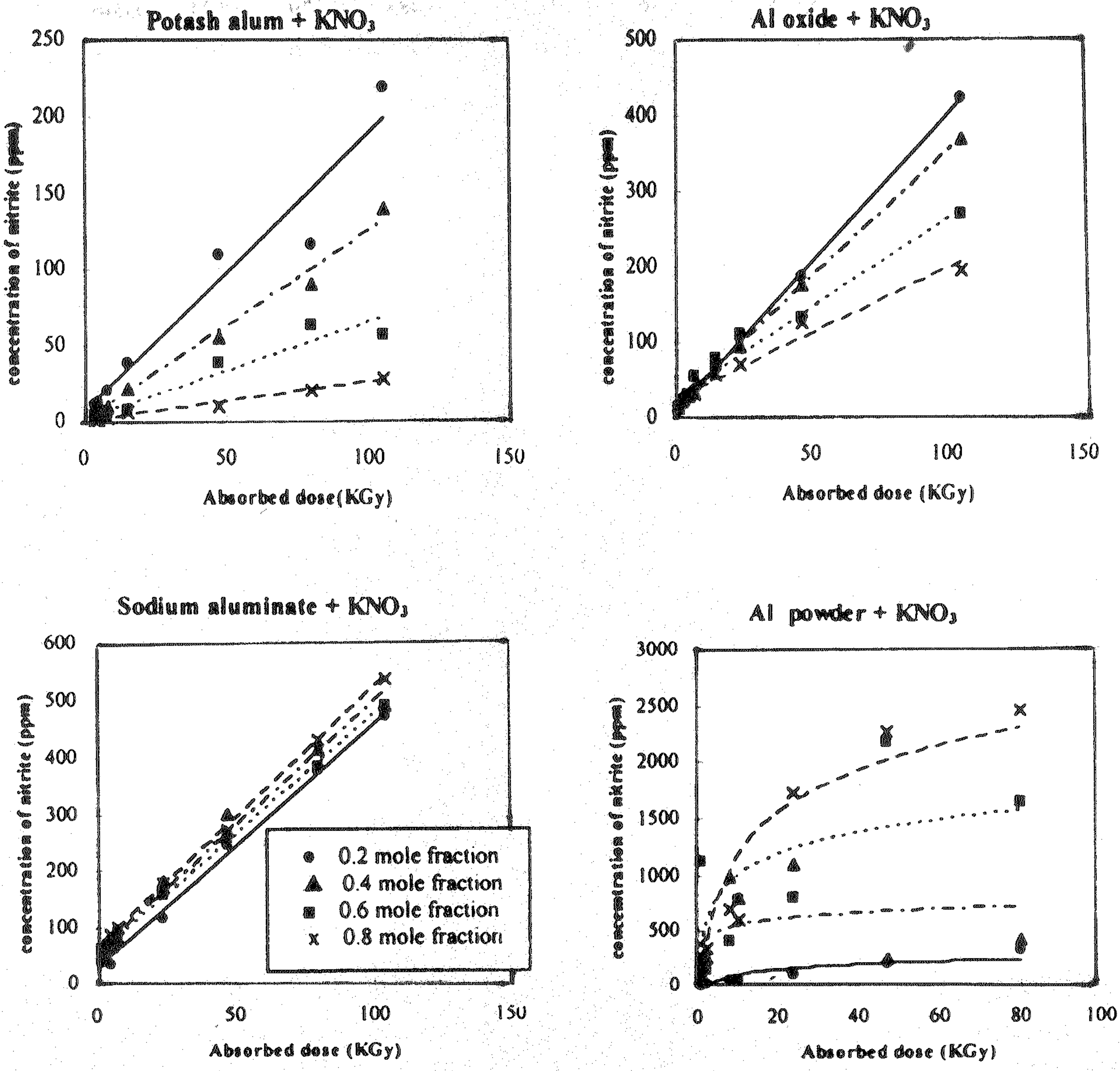

Fig. 1. Variations in concentration of nitrite with varying mole fractions of additives in accordance with dose absorbed

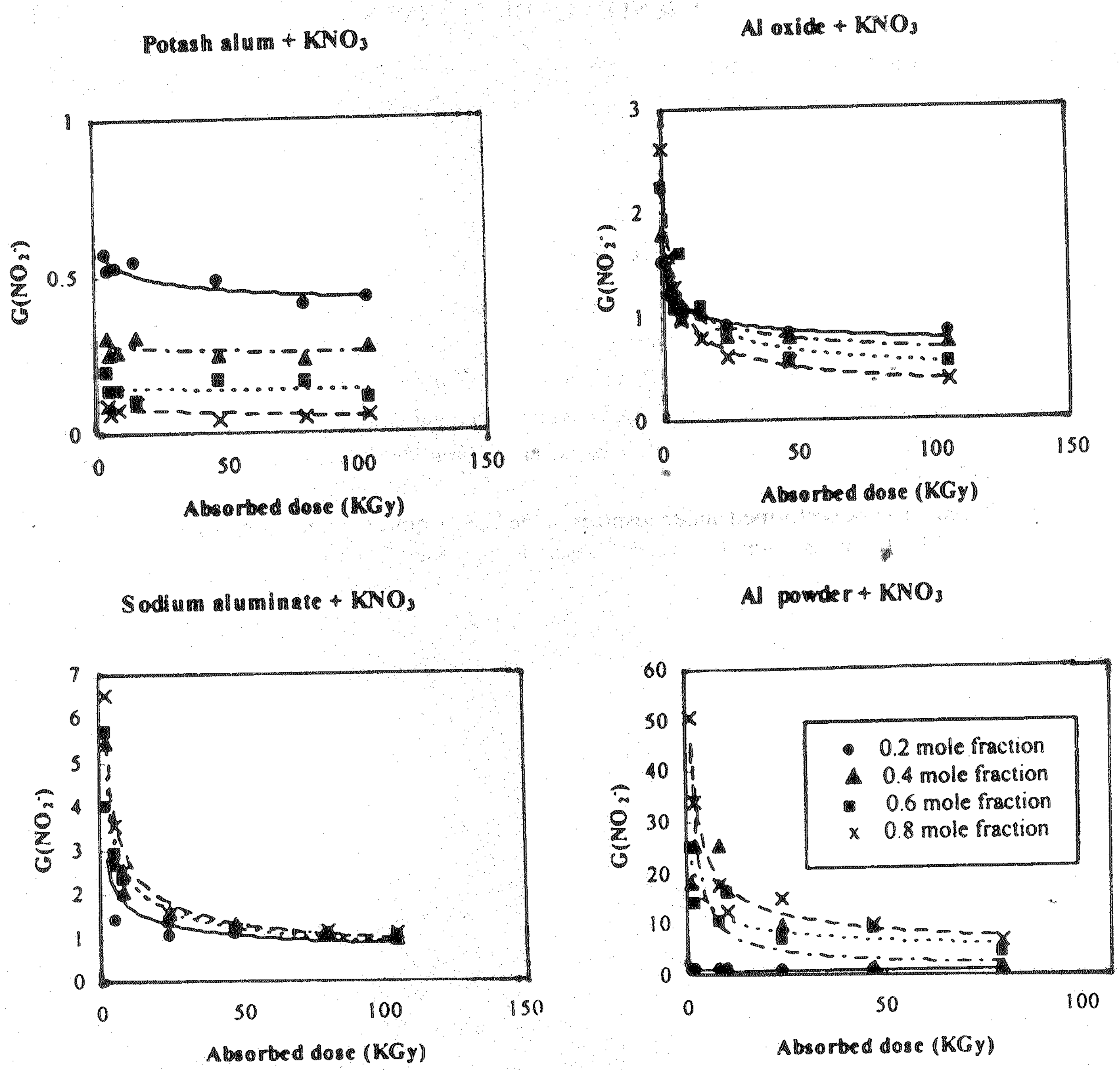

Fig. 2. Variations in $G(NO_2^-)$ with varying mole fractions of additives in accordance with dose absorbed

In case of admixtures of potash alum with KNO_3, 0.2 mole fraction shows higher values as compared to other mole fractions. Patil *et al.*[7] have suggested that higher G values of nitrite observed in case of admixture, the energy absorbed in the bulk of the additive migrates to its surface from where it is effectively transferred to the intimately close nitrate ion where decomposition occurs. As the particle size of potassium nitrate has been kept constant, effective surface area of contact between closely held particles of the constituents might be favouring the transfer of energy leading to increase in G-values. Similarly, the opposite characteristic must be decreasing the G-values, which happens in the case of admixtures of aluminium oxide and potash alum.

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