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Note

REACTIONS OF METAL OXIDES WITH $NO_2(g) + O_2(g)$

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The reactions of a mixture of $NO_2(g) + O_2(g)$ with sixteen metal oxides and two hydroxides have been followed with combined TG + DTA. The fraction reacted (F), was calculated assuming the reaction (nitration) to be

$$MO_{(s)} + 2NO_{2(g)} + \tfrac{1}{2}O_{2(g)} = M(NO_3)_{2(s\text{ or }l)} \qquad (1)$$

but it was recognised that nitrites, basic nitrates, basic nitrites and higher or lower oxides are also possible products. Thermodynamic and decomposition data for many nitrates and nitrites were compiled by Stern [1] in 1972, but there have been very few studies of the rate of formation of nitrates by gas–solid reaction. The only reaction which has received some attention is the nitration of CaO [2–5] by NO_2 or $NO_2 + O_2$, partly because this is a route to $Ca(NO_3)_2$ fertiliser. There are also reports in the literature of nitration of oxides by liquid N_2O_4 [6–8] in sealed ampoules at temperatures up to 150°C. For example, the uranium oxides, UO_2, U_3O_8 and UO_3, have been reacted with liquid N_2O_4 to give $UO_2(NO_3)_2 \cdot N_2O_4$, an adduct of uranyl nitrate, the reaction being relevant to the proposed use of N_2O_4 as a heat-transfer medium in nuclear reactors [8].

The aim of the present work was to evaluate quickly the possibility of reacting $NO_2 + O_2$ with certain oxide components in a metallurgical ore to form anhydrous nitrates which could then be water-leached as part of a metal recovery process.

EXPERIMENTAL

The solids listed in Table 1 were used in the as-received powdered form and were of technical grade except: CaO (99%), $Ca(OH)_2$ (99.9%), MgO (99.99%), UO_2 (99.97%). The O_2 and liquefied N_2O_4 were bottled gases from BOC Ltd. with water contents of 50 and 600 ppm. Liquid N_2O_4 boils at 21°C to give $N_2O_{4(g)}$, which dissociates to 2 $NO_{2(g)}$ above about 100°C [1].

The apparatus for combined TG + DTA in a corrosive atmosphere is described elsewhere [9]. The gas flow system consisted of streams of N_2O_4

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and O_2 which converged before entering the apparatus. The N_2O_4 cylinder and its flow control valve were submerged in a water bath thermostated at 40°C. However, some $N_2O_{4(g)}$ tended to condense in the tubing on its way to the apparatus, so the N_2O_4 flow rates were only approximate. From measurements with a soap-bubble flow meter, $NO_2 + O_2$ mixtures with 5–25% O_2 at total flow rates of about 100 cm^3 min^{-1} were maintained. Thus, the equilibrium constant ($p\mathrm{NO}_2^{-2} \times p\mathrm{O}_2^{-1/2}$ [5]) for reaction (1) was maintained in the range 5–3.5.

Samples of 50 mg were used in the TG and DTA crucibles; the DTA reference crucible was empty. If the sample reacted with the gas at room temperature, the reaction was allowed to continue until its rate became insignificant. Only then was heating begun, at rates of 5–7°C min^{-1} up to 800°C, a temperature high enough to decompose the reaction products.

RESULTS

Table 1 summarises results obtained for sixteen oxides and two hydroxides. In calculating *F*, the fraction reacted, reaction (1) was assumed except for the three uranium oxides, which were assumed to form $UO_2(NO_3)_2$.

TABLE 1

Results for the reactions of several powders with $NO_2 + O_2$

Solid	Maximum fraction converted to nitrate	Decomposition range of product (°C)
Al_2O_3	0	–
Bi_2O_3	0.10	675–700
CaO	0.78, 0.70	550–650, 550–650
$Ca(OH)_2$	1.00	450–550
Cu_2O	0.60	150–300
CuO	0	–
Fe_2O_3	0	–
MgO	0.27, 0.49, 0.40	350–450, 350–450, 325–425
$Mg(OH)_2$	1.00, 1.00	400–450, 375–450
NiO	0	–
PbO	0.33, 0.37	525–650, 525–625
SnO_2	0	–
TiO_2	0	–
WO_3	0	–
ZnO	0.42, 0.75	200–325, 200–325
UO_2	0	–
U_3O_8	1.05, 0.5, 0.73	225–325, 250–275, 225–325
UO_3	1.28, 1.00	200–350, 250–350

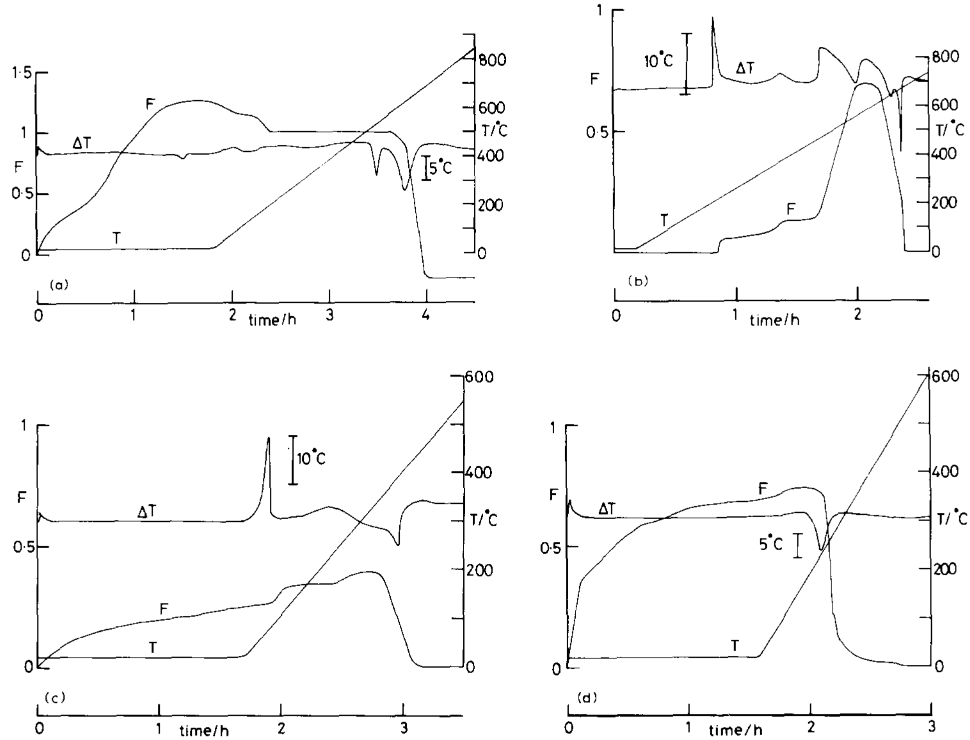

Fig. 1. Thermographs for the reactions of $NO_{2(g)} + O_{2(g)}$ with (a) $Ca(OH)_2$; (b) CaO; (c) MgO; (d) U_3O_8.

Several points are notable. Eight oxides (including UO_2) did not react at all; $Ca(OH)_2$ and $Mg(OH)_2$ were completely converted; UO_3 and U_3O_8 were completely converted in some experiments; the remaining oxides reacted incompletely. The thermographs (examples in Fig. 1) were generally complicated indicating the probable involvement of nitrites, etc. Apart from the obvious correlation of weight increases and decreases with exotherms and endotherms (nitration is exothermic), only a few comments can be made. The endotherms in Fig. 1a and b around 550°C correspond to the melting of $Ca(NO_3)_2$ [1], and the appearance of the reacted solid confirmed this. In contrast, $Mg(NO_3)_2$ does not melt. Figure 1a is consistent with the sequence $Ca(OH)_2 \rightarrow ? \rightarrow Ca(NO_3)_{2(s)} \rightarrow Ca(NO_3)_{2(l)} \rightarrow CaO$. Figure 1d shows the high reactivity of U_3O_8 at room temperature.

Reasons for the poor reproducibility of many of the results could include the effects of H_2O on the reactions and the variations in NO_2 flow rates.

CONCLUSIONS

The most reactive oxides were U_3O_8 and UO_3. However, UO_2, a major component in uranium oxide ores, did not react, so it is not feasible to extract uranium by forming an anhydrous nitrate. No other oxides reacted in a way which could be exploited in extractive metallurgy.

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