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Low temperature incineration of mixed wastes using bulk metal oxide catalysts

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Abstract

Volume reduction of low-level mixed wastes from former nuclear weapons facilities is a significant environmental problem. Processing of these materials presents unique scientific and engineering problems due to the presence of minute quantities of radionuclides which must be contained and concentrated for later safe disposal. Low-temperature catalytic incineration is one option that has been utilized at the Rocky Flats facility for this purpose.

This paper presents results of research regarding evaluation of bulk metal oxides as catalysts for low-temperature incineration of carbonaceous residues which are typical by-products of fluidized bed combustion of mixed wastes under oxygen-lean conditions. A series of 14 metal oxides were screened in a thermogravimetric analyzer, using on-line mass spectrometry for speciation of reaction product gases. Catalyst evaluation criteria focused on the thermal–redox activity of the metals using both carbon black and PVC char as surrogate waste materials. Results indicated that metal oxides which were P-type semiconductor materials were suitable as catalysts for this application. Oxides of cobalt, molybdenum, vanadium, and manganese were found to be particularly stable and active catalysts under conditions specific to this process ($T < 650°C$, low oxygen partial pressures).

Bench-scale evaluation of these metal oxides with respect to stability to chlorine (HCl) attack was carried out at 550°C using a TG/MS system. Cobalt oxide was found to be resistant to metal loss in a HCl/He gaseous environment while metal loss from Mo, Mn, and V-based catalysts was moderate to severe. XRD and SEM/EDX analysis of spent Co catalysts indicated the formation of non-stoichiometric cobalt chlorides. Regeneration of chlorinated cobalt was found to successfully restore the low-temperature combustion activity to that of the fresh metal oxide.

Keywords: Low temperature incineration; Mixed wastes; Bulk metal oxide catalysts

1. Introduction

Volume reduction and safe disposal of wastes from former nuclear weapons processing facilities is a major environmental concern in the United States. For many years, the Rocky Flats plant near Golden, Colorado acted as the primary producer of plutonium triggers for nuclear warheads, but in January 1992 switched to a clean-up and environmental restoration facility [1]. Large volumes of chemically hazardous substances with sometimes minute levels of radionuclides (Pu, U, Am) have been accumulated on sight at Rocky Flats. This type of material is collectively referred to as low-level mixed waste because of its heterogeneity and often unknown origin. A typical characterization of mixed waste from Rocky Flats is summarized in Table 1.

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Table 1
Rocky flats mixed waste characterization [2]

Waste component	Relative amount (wt%)
Wood/paper/cloth	27.7
Chlorinated oils	20.0
Solidified organics	13.7
Latex	12.2
Polyvinylchloride	8.0
Polystyrene resins	6.5
Polyethylene	6.3
Ash/refractory oxides	4.3
PCB liquids	1.1
Other	0.2

This mixed waste stream contains almost entirely combustible materials with high levels of chlorinated substances.

1.1. Fluidized-bed incineration at rocky flats

A key problem surrounding high temperature thermal treatment of radioactive material involves the formation of volatile radionuclide species. Studies have demonstrated that both plutonium and uranium can form oxyhydroxide, oxychloride, and hydride species above 900°C that remain volatile at low temperatures [3,4]. A low temperature catalytic fluidized bed incineration unit (FBU) with a capacity of 82 kg/h began operation at Rocky Flats in 1977 for processing mixed waste generated on-site. Volume reduction of combustible mixed waste materials was accomplished leaving an ash composed of heavy metals, carbon (char), refractory oxides, and radionuclides. Volume reduction capabilities were greater than 40:1 for typical plant solid mixed waste [5]. A chromia on alumina (CrO_3-Cr_2O_3/Al_2O_3) catalyst was used in the Rocky Flats FBU to accelerate the rate of combustion. Addition of this catalyst to the FBU met with mixed success. Pyrolysis vapors and gaseous combustion intermediates could be readily oxidized at low temperatures, but carbonaceous deposits continued to build up in FBU ash [6–8]. Additionally, the presence of hexavalent chromium (Cr^{6+}) in this material presented additional hazardous waste concerns [9]. Research at Rocky Flats demonstrated that carbon residue and hexavalent chromium in the ash material could severely disrupt the cement matrix which was utilized as a residue encapsulation process.

Following extensive research, the DOE revisited incineration in 1990, deeming it the best 'operational technology' for thermal treatment and volume reduction of mixed waste [10]. A research team consisting of technical personnel from Rocky Flats, CSM, and West Virginia University (WVU) was assembled to assist in design and development of a new fluidized bed reactor system that would be suitable for volume reduction of mixed wastes. Researchers at WVU subsequently recommended that Rocky Flats investigate construction of a hybrid fluid bed reactor. This unique reactor incorporated both a bubbling bed and entrained flow zones which allowed catalyst and sodium carbonate (used as an in-situ HCl sorbent) to be easily added, regenerated and recycled. As designed, the bubbling bed section was to be operated in an oxygen-lean manner ($< 10\%$ oxygen) in order to control combustion and prevent a temperature excursion that could result in volatilization of radioactive components. A schematic of the WVU design is shown in Fig. 1.

The goal of this research project was to identify, test, and analyze bulk metal oxides that could potentially be utilized as catalytic materials for low temperature incineration of mixed waste. Experimentation will focus on low temperature combustion of solid waste surrogate materials which are representative of FBU carbonaceous residues in the presence of bulk metal oxides. Selection criteria for replacement catalysts include: (1) a high affinity for solid carbon residue combustion at low temperature (400–700°C) as well as (2) the ability to act as redox catalysts. The rationale for this latter criteria is due to the nature of the hybrid reactor design (Fig. 1), where the bubbling bed section is presumed to be operating under oxygen-lean

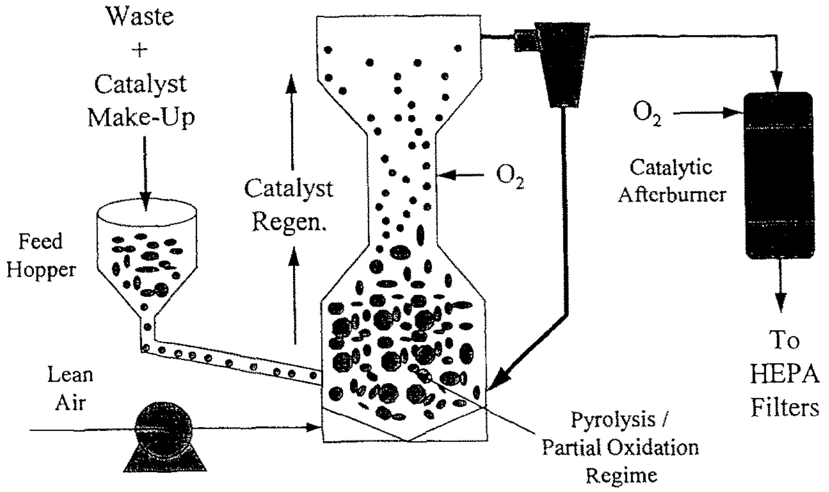

Fig. 1. Schematic of hybrid fluidized bed reactor.

conditions. Hence redox activity is desirable for the catalyst to be effective for char combustion.

2. Literature review

Work on fluidized-bed incineration of radioactive waste material at Rocky Flats began in 1972. Laboratory scale combustion of typical plant waste material was investigated using a vertically staged system of fluidized bed reactors operating at 500–600°C. Several supported catalysts were tested in the second stage fluid-bed but chromia on alumina (CrO_3-Cr_2O_3/Al_2O_3) provided the best combination of HCl resistance, low operating temperature (550–600°C), and PIC conversion [11]. The lean oxygen conditions required for bed temperature control increased the carbon content of the ash material to more than twice that seen when using air as the fluidization gas [6,7].

Following the success of fluidized-bed bench scale testing, a demonstration unit was built at Rocky Flats by Rockwell International in 1977. This pilot system was composed of two fluidized-bed reactors with a waste throughput of 82 kg/h operating between 525–600°C. A schematic of the fluidized-bed unit (FBU) is presented in Fig. 2. Shredded solid waste or slurry entered the primary reactor (R1) via a screw feeder from a waste hopper where it was pyrolyzed and partially combusted under lean oxygen conditions in a bed of Na_2CO_3 and chromia on alumina oxidation catalyst. The Na_2CO_3 sorbent acted as a scavenger for HCl generated from the degradation of chlorine-containing materials in the waste feed. Pyrolysis vapors and PICs passed on to the secondary reactor (R2) containing only oxidation catalyst. The combination of catalyst and excess oxygen in R2 was sufficient to oxidize more than 99% of PICs in the primary stage flue gas. All entrained fines from both R1 and R2 were removed using cyclones. The final exhaust treatment train for the R2 flue gas consisted of sintered metal filters, a high temperature catalytic afterburner, and five banks of HEPA filtration to remove particulates above 0.3 μm. The concentrated unburnable ash remaining from the fluid beds and cyclones was ultimately sent by conveyor to cement encapsulation processes [5–7,12,13].

In the early 1980s, the Rocky Flats demonstration FBU successfully destroyed 21 500 kg of low-level solid mixed waste and more than 5600 l of liquid plant waste. A trial test burn of the unit under EPA supervision was made in 1981 using a poly-chlorinated biphenyl (PCB)

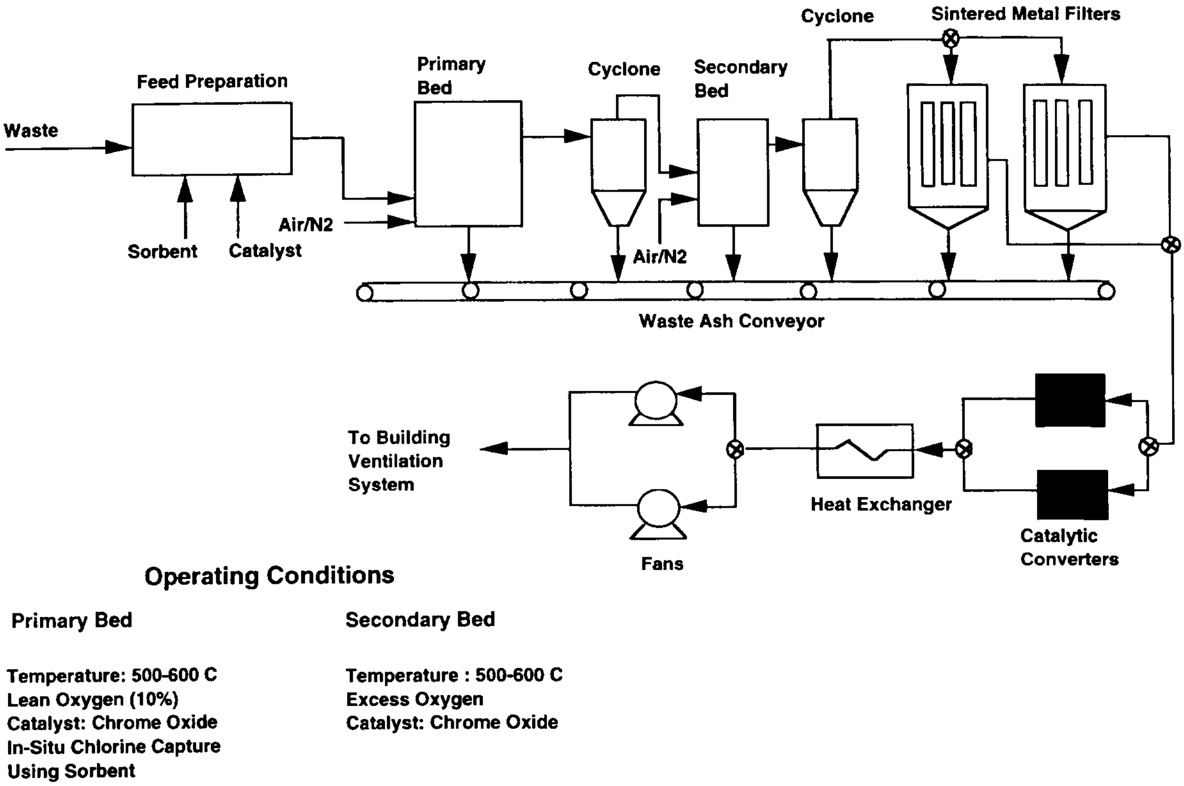

Fig. 2. Rocky flats fluid bed incineration unit.

and trichlorobenzene (TCB) liquid feed. During EPA supervised tests, a destruction and removal efficiency greater than 99.9999% was obtained for all waste components [14,12]. Fluidized-bed catalytic combustion of low-level hazardous organic mixed waste has also been extensively researched in Russia using doped perovskite ($CuMgCr_2O_7/Al_2O_3$) catalysts [15].

Combustion of solid carbonaceous material has been studied extensively by many researchers for application to catalyst decoking and regeneration [16–18], commercial solid waste incineration [19], as well as coal and coke oxidation [20–22]. The technique of thermogravimetric (TG) analysis has been used by several researchers for screening the oxidation activity of various transition metal oxide catalysts for low temperature combustion of graphite/amorphous carbon black [23,24] and removal of soot from diesel engine exhaust [25].

The effects of metallic impurities and metal oxides in enhancing the oxidation of solid carbonaceous fuel by gaseous oxygen is well known. Many researchers have documented and tried to explain this effect on a variety of fuels including graphite/activated carbon [26–28], exhaust soot from diesel engines [24,25,29,30], petroleum coke [22], and peat [31,32].

3. Experimental

All experiments were carried out in a Seiko SSC5200 model TG/DTA thermal analysis system. A Fisons-VG quadrupole mass spectrometer was utilized for speciation of reaction product gases. Identification of fragmentation patterns was carried out using the Fisons Post Soft data conversion software, and the NIST Mass

Spectral Library [33]. Reagent gases and custom gas mixtures utilized for balance purge and reaction were industrial grade and were supplied by General Air of Denver, CO. Preparation of PVC char was accomplished by pyrolysis (helium bath gas) of PVC in a horizontal tube furnace to a final temperature of 900°C. High purity medium molecular weight PVC powder from Aldrich Chemical was used as the starting material. A heating rate of 5°C/min was used with isothermal holds at 50°C intervals to produce the char. Elemental analysis of the char showed that it consisted of approximately 94% fixed carbon, 2% hydrogen, 0.01% nitrogen, with traces of chlorine (570 ppm), Si (0.15%), Al (0.02%) V (70 ppm) and Ni (20 ppm). Other experimental details are available [34].

4. Results and discussion

The goal of this research was to find a bulk metal oxide material that would be active as a catalyst for low-temperature combustion of carbonaceous residues resulting from pyrolysis and partial oxidation of polymeric materials such as PVC. Carbon black and PVC char were utilized as surrogate waste materials for catalyst evaluation. In order to be useful in the Rocky Flats hybrid reactor, the catalysts should be able to function as redox agents, giving up their oxygen in the oxygen-lean bubbling bed zone and being regenerated and recycled in the oxygen-rich entrained-flow and disengaging zones.

A sample thermogram for the combustion of PVC pyrolysis char in 10% O_2 with a 10°C/min

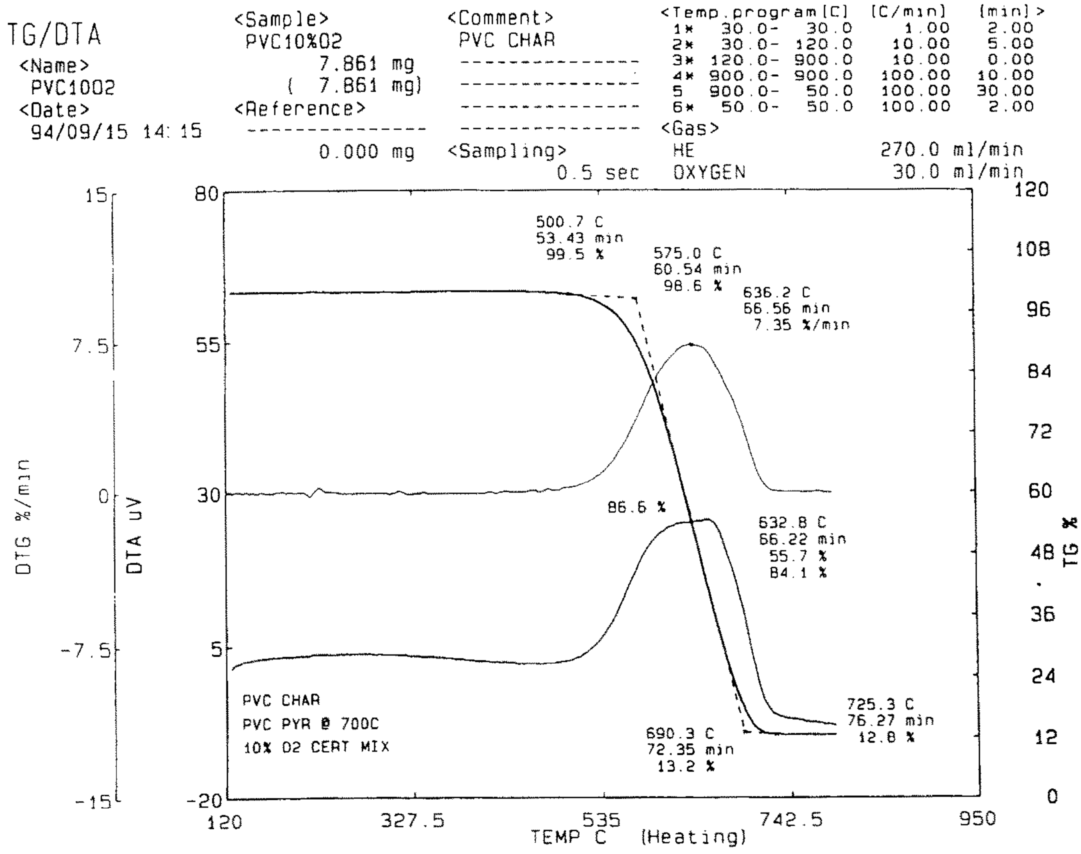

Fig. 3. Sample thermogram for PVC char combustion.

heating rate is presented in Fig. 3. Conversion rate (percent weight loss per minute) is also provided on the thermogram in the form of the DTG (differential thermogravimetry) curve by numerical differentiation of conversion data with respect to run time. The utility of the DTG trace can be seen in its ability to amplify slope changes and clarify inflection points on the TG curve. Finally, sample heat effects are measured by the differential thermal analysis (DTA) curve. It is easy to see from this figure that PVC char combustion can be characterized as a single step exothermic process because of the single symmetric DTG peak and positive DTA baseline deviation

Two key parameters from a TGA thermogram can aid in characterizing the thermal degradation of a solid material. The lower thermal stability limit of a substance, known as the reaction initiation temperature (T_i) occurs when sample weight loss begins. For the sake of consistency, T_i is usually defined as the temperature when the slope (conversion rate from DTG curve) of the TG curve exceeds a particular threshold value such as 0.001–0.1%/min weight loss. Another characteristic point, known as the maximum conversion rate temperature (T_m), occurs when the maximum value is reached on the DTG curve. Applying these definitions to the PVC char thermogram, weight loss initiation occurs at $T_i = 501°C$ with a maximum weight loss rate at $T_m = 636°C$. Combustion stops near 725°C leaving a residue which is 12.8% of the initial sample weight.

These parameters (T_i and T_m) can be used as evaluative measures for the effectiveness of a catalyst. Fuel combustion becomes more favorable at a lower temperature and faster rate as initiation temperature is lowered and T_m approaches T_i. Hence, comparison of catalyzed and uncatalyzed degradation kinetics of surrogate waste materials was carried out using T_i and T_m as measures of catalyst oxidation activity. Prior to initiation of catalyst screening, reproducibility studies were conducted for graphite combustion in 2% O_2, PVC pyrolysis, and PVC oxidation in 10% O_2. Standard deviations less than 4°C in T_i and T_m for all measurements were found to be characteristic of the data.

4.1. Bulk metal oxides: redox testing

The oxygen availability of bulk transition metal oxides was first tested using carbon black as a surrogate waste fuel under pyrolysis conditions in the TGA. The goal of such a procedure was to establish which oxides could give up their own lattice oxygen via the thermal–redox cycle to initiate combustion of a carbonaceous fuel sample in an inert reaction gas environment. Metal oxides demonstrating this ability would have highly mobile lattice oxygen as well as low transitional energy barriers between metal cation oxidation states. Using T_i and T_m as measures, the temperature window of activity and metal cation reducibility (small $T_m - T_i$) of the oxide could be evaluated.

TGA testing was conducted on 14 transition metal oxides using a carbon black/catalyst mixing ratio of 1 mole C to 1 mole O_2 in the oxide under pyrolysis conditions (300 sccm N_2). Sample weight loss and identification of CO_2 in TGA off-gases with on-line mass spectrometry were used as indicators of carbon black combustion. The onset of combustion was verified by a corresponding increase in signal intensity of the 44 AMU molecular ion peak for CO_2 in sample off-gases.

Catalyst metal oxide semiconducting properties are shown in Table 2, and redox activities are presented in Table 3.

Overlays of TG/DTG data for redox active metal oxides are shown in Fig. 4 and Fig. 5. As can be seen, the DTG curves show that some bulk oxides such as MnO_2 and Co_3O_4 release their lattice oxygen in a stair-step manner at different temperatures and rates while others liberate oxygen for combustion in one single process (PdO). The sharp weight loss in the MoO_3 TG curve at 830°C was a result of catalyst volatilization after melting at 795°C as opposed to oxygen release.

Table 2
Carbon black pyrolysis studies with bulk metal oxides

Redox active oxides	Oxide type	Redox inactive oxides	Oxide type
Co_3O_4	P	NiO	P
CuO	P	WO_3	Lattice
MnO_2	P	Cr_2O_3	N
MoO_3	Lattice	Nb_2O_5	N
PdO	N	TiO_2	N
Fe_2O_3	N	V_2O_4	N
		ZnO	N
		ZrO_2	N

Table 3
Activity ranking: bulk oxides via redox mechanism

Ranking	Metal oxide	T_i (°C)	Ranking	Metal oxide	$T_m - T_i$ (°C)
1	MnO_2	480	1	MnO_2	70
2	MoO_3	515	2	PdO	100
3	CuO	520	3	Co_3O_4	117
4	PdO	580	4	MoO_3	140
5	Co_3O_4	660	5	CuO	265
6	Fe_2O_3	755	6	Fe_2O_3	n/a

A more quantitative comparison of catalyst redox activity can be made if T_i and T_m from initial sample weight loss are introduced. Ranking schemes for the 6 redox active metal oxides based on these measures are provided in Table 3 using a TG slope initiation threshold of 0.001%/min weight loss.

Since conclusions regarding metal oxide activity change with ranking method, it is apparent that T_i and $T_m - T_i$ provide different measures of catalyst functionality. Initiation temperature tends to reflect a lower limit of effective catalyst operation while $T_m - T_i$ gives an assessment of catalyst metal cation reducibility. Conceptually, oxidation state transitions in the metal oxide should be more kinetically favored when $T_m - T_i$ is small. As a result, catalysts showing a low initiation temperature and small

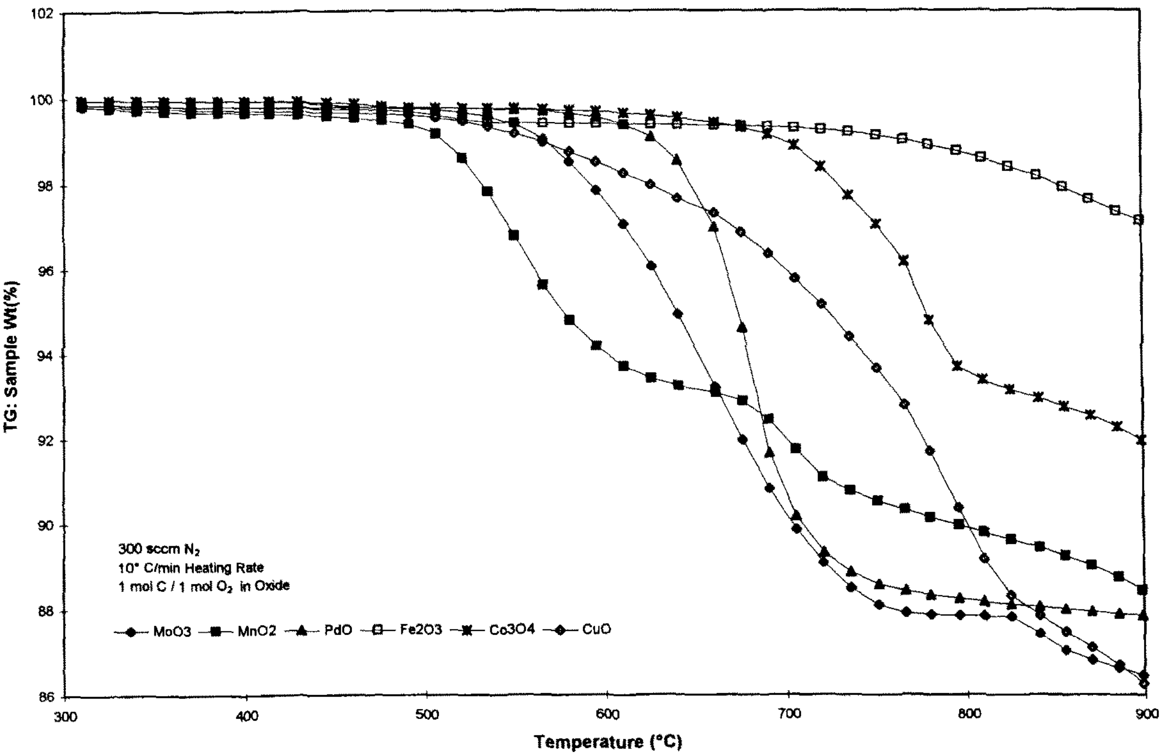

Fig. 4. Thermograms for redox-active metal oxides.

$T_m - T_i$ temperature gap should be best suited for low temperature controlled oxidation of carbonaceous material in the oxygen-lean stage of the Rocky Flats FBU. A bulk oxide like MnO_2 would be potentially very active because lattice oxygen release occurs at a low temperature (480°C) and at a considerable rate (lowest $T_m - T_i$).

Information from the literature suggests that N-type vanadium oxides may also exhibit redox behavior. Based on this premise, V_2O_3, V_2O_4, and V_2O_5 were tested with PVC pyrolysis char using a mixing ratio of 5 mole C to 1 mole metal ion under pyrolytic conditions (275 sccm He). A blank PVC char sample with no catalyst was pyrolyzed in the TGA before oxide testing to affirm that the surrogate waste fuel was inert. Despite difficulties in comparing carbon black combustion with PVC char combustion, results showed that V_2O_5 was redox active below 700°C while V_2O_3 and V_2O_4 were found to be thermally inert.

One important property which plays a role in redox activity is metal oxide semiconductor type. With one notable exception (NiO), all P-type oxides tested in TGA pyrolysis studies show redox activity for char combustion. Numerous researchers have identified that the multiple stable oxidation states and high concentration of positive 'holes' in P-oxides foster surface oxygen mobility to a greater extent than N-oxides. Each 'hole' provides a vacancy where the free electrons of mobile surface oxygen species can be stabilized. In order for NiO to release its chemical oxygen, the Ni^{2+} cations must be reduced to Ni^0 since nickel can not exist in the +1 oxidation state (Anderson 1989). However, it is well known that nickel can only be reduced to its metallic state with H_2 or CO at high temperatures [35]. For this reason, the redox inactivity of NiO can be well understood.

Other questions arise when trying to explain why three N-oxides (Fe_2O_3, PdO, V_2O_5) are redox active under these conditions when previ-

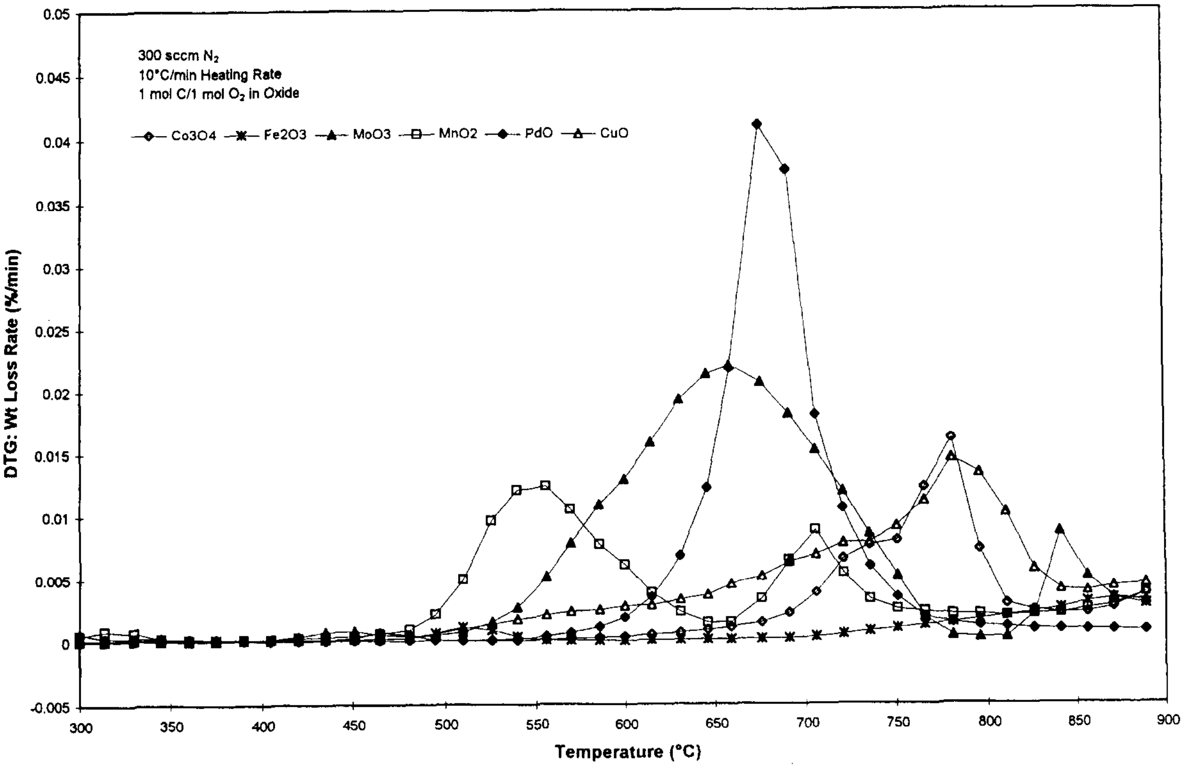

Fig. 5. Differential thermograms (DTG) for redox-active metal oxides.

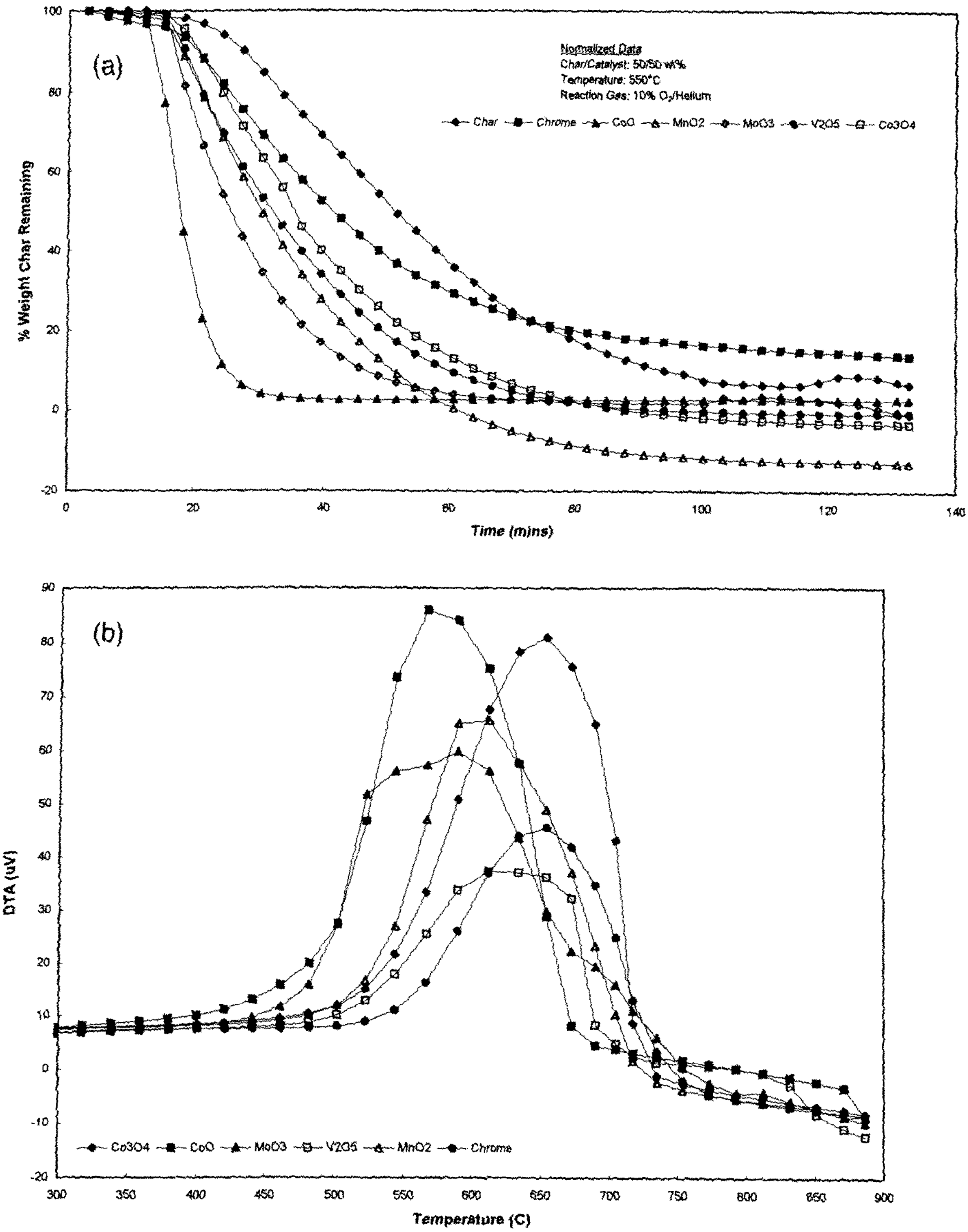

Fig. 6. (a) Isothermal activity testing with PVC char. (b) Non-isothermal differential thermal analysis results.

ous research has shown that, in general, all N-oxides are thermally stable and have low oxygen availability. When trying to understand this behavior, it is instructive to consider some quantitative information on oxide semiconductor properties and oxidation state transition energy barriers (Table 4).

Among the N-type oxides tested, PdO and Fe_2O_3 have the lowest semiconductor band gap energies and oxide formation heats. Since band gap reflects the energy barriers to charge stabilization in the crystal lattice, N-oxides having low barriers can more easily distribute cationic charge imbalances that occur when oxygen is removed from the lattice. Also, low oxide formation heat suggests that small energy barriers exist between stable metal cation oxidation states. Therefore, PdO and Fe_2O_3 may show redox activity because of low oxidation state transition energies and the ability to stabilize cation charge imbalances that occur when the metal oxide is reduced by the carbon fuel.

4.2. Evaluation with PVC char: application to mixed waste combustion

A summary evaluation of the bulk metal oxide catalysts tested based on redox activity temperature range for carbon black combustion is provided in Table 5. For application to fluidized bed combustion of mixed waste, Fe_2O_3 can be eliminated based on insufficient low temperature activity. Palladium oxide was eliminated due to excessive cost ($300/g). The remaining catalysts were tested for activity towards combustion of PVC char in the Seiko TGA/DTA. Results of isothermal activity testing are shown in Fig. 6a, while DTA data from non-isothermal testing are given in Fig. 6b. As can be seen clearly from the DTA information, CoO is the most active of these candidate metal oxides in the temperature range of applicability.

Table 4
Chemical properties of some N-oxides

Metal oxide	Band gap energy [a] (eV)	Oxide formation heat [b] (kJ/mol O)
PdO	1.0	−85
Fe_2O_3	1.9	−275
V_2O_5	2.2	−310
Cr_2O_3	3.3	−380
ZnO	n/a	−348
TiO_2	3.0	−470
Nb_2O_5	3.9	−380

[a] [36].
[b] [37].

Table 5
Bulk oxide temperature activity ranges

Bulk oxide	Temperature activity range (°C)
MnO_2	475–700
MoO_3	550–725
V_2O_5	600–700
PdO	600–750
CuO	625–825
Co_3O_4	675–825
CoO	500–600
Fe_2O_3	750–900

4.3. Deactivation by HCl and regeneration

During the initial stages of PVC thermal degradation, large quantities of chlorine are released as HCl, hence it is possible for the catalyst to compete with sorbent material as a chlorine scavenger. Thus, resistance to deactivation by chlorine is an important property of the material that is to be used as a catalyst in this application. Prior research had shown copper to be susceptible to chlorine attack [6] with massive metal loss resulting from the formation of copper chloride ($CuCl_2$). The remaining materials identified above from the screening study were subjected to exposure to a flowing gas containing 2% HCl in helium for up to 16 h at 550°C. These experiments were carried out in a CAHN model TG-131 thermogravimetric analyzer so that the weight change could be monitored continuously. Heating in helium in the absence of HCl resulted in no weight change for these metal oxides. Oxides of molybdenum, vanadium, and manganese all lost weight upon

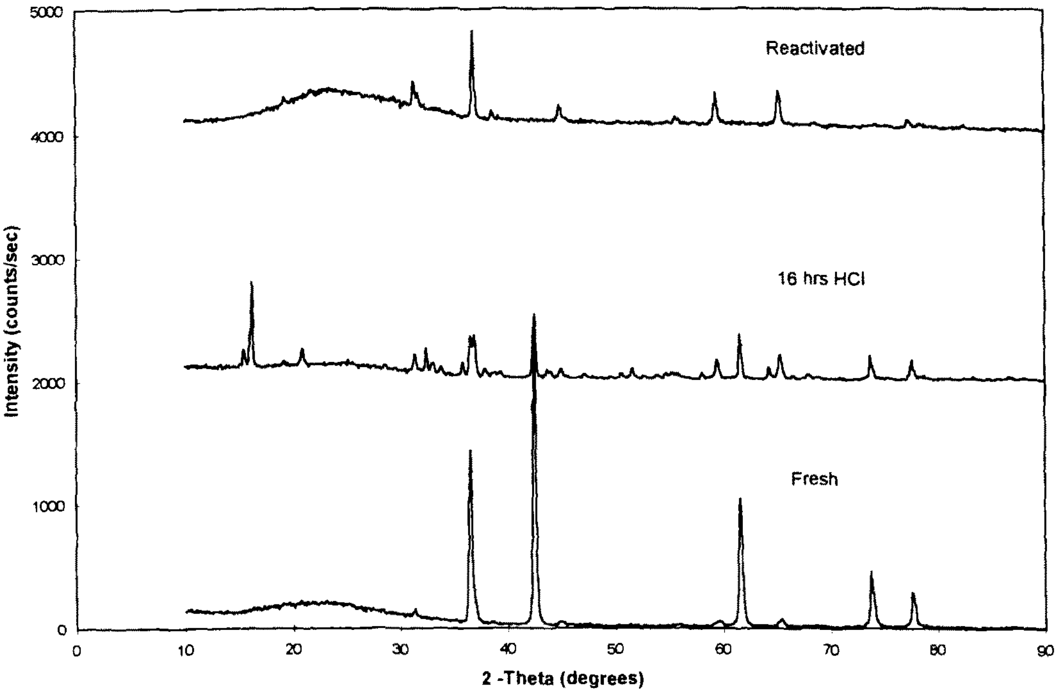

Fig. 7. XRD of fresh, chlorine poisoned, and reactivated CoO.

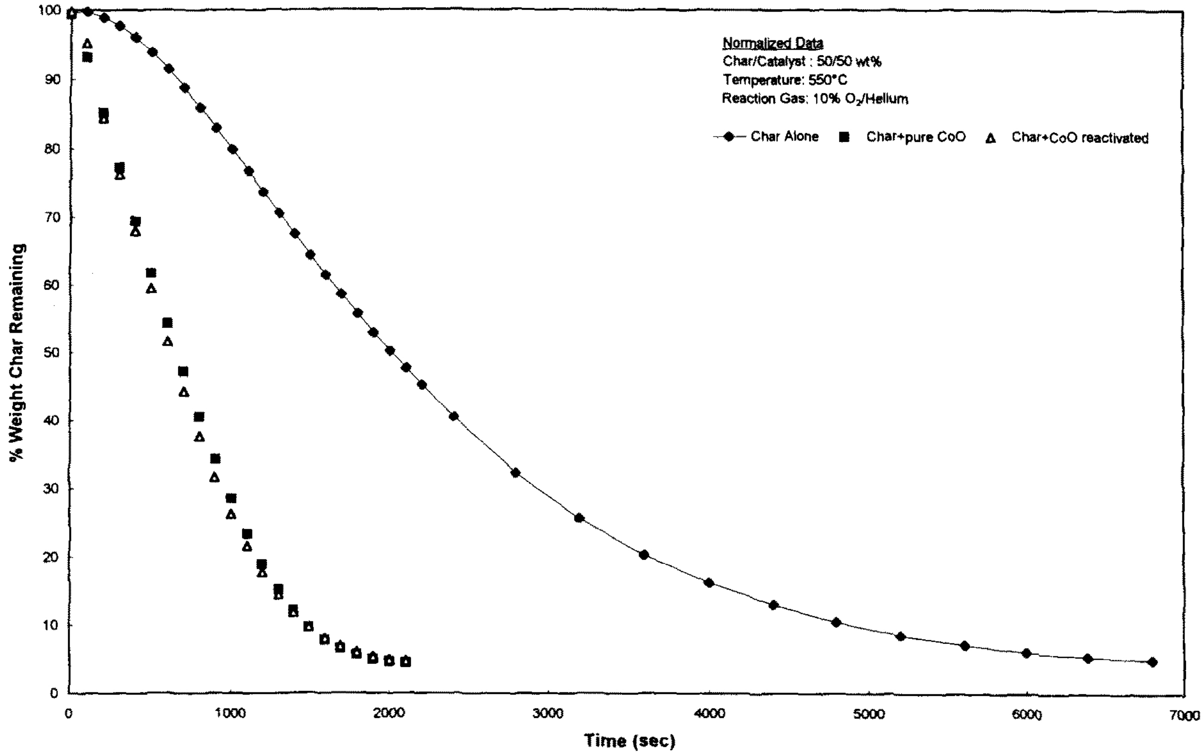

Fig. 8. Comparison of char combustion activity for fresh and reactivated CoO.

exposure to gaseous HCl due to the formation of volatile metal chlorides and oxychlorides, while cobalt oxide (CoO and Co_3O_4) both gained weight indicating the formation of stable chlorides. For the catalyst with the best low temperature char combustion activity (CoO), the formation of metal chlorides was confirmed by XRD analysis (peaks at $2\theta \cong 15$ in Fig. 7). As shown in Fig. 8, reactivation of the chlorine-contaminated catalyst by exposure to a 10% oxygen stream at 550°C for 3 h was sufficient to restore activity to that of the original oxide although the XRD analysis of the regenerated catalyst suggested that the original chemical form of the oxide material had not been recovered (Fig. 7).

5. Conclusions

Several bulk oxides have been identified that could function as low-temperature catalysts for incineration of mixed wastes. P-type semiconducting bulk oxides (Co_3O_4, MnO_2, MoO_3, and V_2O_5) have been found to promote catalytic oxidation of carbonaceous residues through the thermal–redox cycle by releasing lattice oxygen to initiate combustion under pyrolytic conditions in the 450–600°C temperature range. N-type bulk oxides do not exhibit redox activity to any great extent under these conditions of temperature and reaction environment because surface oxygen mobility is too low. In general, highly mobile lattice oxygen from many stable metal cation oxidation states, low surface oxygen binding energy, and small semiconductor band gap are requirements for redox type activity under these conditions. Cobalt oxide (CoO) shows particular promise for utilization as a bulk oxide catalyst for combustion of mixed wastes in a two-stage hybrid fluidized bed reactor due to its superior low-temperature activity for combustion of PVC char, and resistance to deactivation by chlorine.

Acknowledgements

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