

# The Growth, Structure and Surface Chemistry of Oxide Films as Model Catalysts

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"...the best long-range strategy (in all fields of catalysis research) is twofold: to carry out research for the discovery of new, advanced catalysts and catalytic materials, and to focus fundamental research on the elucidation of catalytic sites and catalytic reaction mechanisms at the atomic/molecular level" [Advanced Heterogeneous Catalysts for Energy Applications, G. A. Mills, *et al.*, DOE/ER-30201-H1, April 1994]. The present paper will describe recent results from our relatively new program to perform detailed studies of the catalytic properties of metal-oxide materials; in particular, to effect a determination of the active catalytic site(s) and the mechanism for reactions over this especially important class of heterogeneous catalysts. Issues of structure-sensitivity, poisoning and promotion, and competing reaction mechanisms are critical questions that need to be addressed in a detailed manner for catalysis by oxides. As just one important example, both surface (Langmuir-Hinshelwood) and direct (Eley-Rideal) reaction mechanisms have been proposed for the Selective Catalytic Reduction (SCR) reaction of nitrogen oxides ( $\text{NO}_x$ ) over vanadia/titania catalysts. For this program we are using a number of unique, state-of-the-art capabilities available in the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory; for example, the first molecular beam epitaxy (MBE) system dedicated to the growth of model metal-oxide films, and a unique high-pressure catalytic reactor/surface science apparatus. The research in the EMSL is specifically focussed on DOE needs to cleanup and restore a large number of contaminated sites that are a legacy of 50 years of nuclear weapons production. It can be expected that catalytic processes will play a major role in the cleanup of DOE sites, and that oxide-catalyzed reactions are likely to be particularly important. Therefore, we have initiated EMSL research programs that are performing molecular-level studies of oxide-catalyzed reactions and we describe some of these in this paper.

## I. INTRODUCTION

### I.1. Catalysis by Oxides:

The critical role that catalysis plays in two of the largest US industrial segments, chemicals and petroleum processing, has been discussed at length in recent reports from the National Research Council [1] and the Department of Energy [2]. In these and other industries, catalytic processes are used as lower-cost, more energy efficient and/or pollution control technologies. Of these processes, a significant number are of particular interest to the missions of the Department of Energy (DOE), specifically with reference to energy production and efficient use, as well as the prevention or remediation of environmental insults. For the purposes of the present paper, three specific examples can be cited. Important examples in the environmental remediation area are the control of  $\text{NO}_x$  emissions derived from the processing of hazardous wastes from storage tanks at the Hanford site near Richland, Washington and elsewhere, and the problems of large quantities of chlorinated hydrocarbons in storage tank wastes and in contaminated soils and groundwater at a number of DOE sites around the country. Efficient processing of petroleum for fuels and other chemical feedstocks is of obvious relevance to the DOE's energy missions. These three examples are briefly elaborated on next with particular emphasis on the problem of  $\text{NO}_x$  emissions.

*I.1.A. Gaseous emissions of  $\text{NO}_x$  from tank waste processing:* Nitrogen oxides,  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ), are some of the most common and most dangerous pollutants of the atmosphere. Stringent regulations have been and continue to be legislated to control these pollutants from stationary (*e.g.*, power plant) and mobile (*e.g.*, automobile) sources. Because of this situation, the need for stepped-up research efforts at both the fundamental and applied levels, with a goal to develop improved  $\text{NO}_x$  emission treatment technologies, has been emphasized in a number of places recently [1-4]. Gaseous  $\text{NO}_x$  emissions are of particular concern to the Office of the Assistant Secretary for Environmental Restoration and Waste Management (OEM) of the DOE in general, and the Hanford site in particular, because of the presence of large quantities of nitrite and nitrate anions in mixed wastes stored in underground tanks, as well as those discharged directly to the soils [5-6]. Treatment of these wastes will most likely involve the generation of gaseous  $\text{NO}_x$  emissions that will have to be secondarily treated to prevent their release to the atmosphere. Of additional concern to DOE and Hanford is the proposed utilization of a number of high-temperature processes for conversion and/or stabilization of much of the underground storage tank wastes, with high-level waste vitrification being just one example. Such processes have the potential to *generate* significant

amounts of NO<sub>x</sub> emissions by well-understood high temperature combustion reactions involving atmospheric nitrogen and oxygen [3]. These 'secondary' NO<sub>x</sub> emissions will also need to be controlled. Presently, compliance with clean air standards is often accomplished by catalytically altering the exhaust emissions. It is quite clear, however, that the current catalyst technologies are insufficient for meeting future regulatory requirements [2,4].

The technologies for treating NO<sub>x</sub> emissions are quite different for the two cases of mobile and stationary sources. In an automobile, NO<sub>x</sub> is reduced by CO and/or unburned hydrocarbons over a three-way catalyst consisting of the precious metals Pt, Pd and/or Rh [4]. In contrast to the automotive (mobile source) case, NO<sub>x</sub> emission control from stationary sources such as power plants is typically accomplished by selective catalytic reduction (SCR) with NH<sub>3</sub> over tungstate/titania or vanadia/titania catalysts [3]. However, a recent DOE study [2] specifically emphasized that "research is needed to understand better the fundamental nature of active sites and reaction pathways [of SCR] in order to make improvements in this developed technology". This is due, in part, to the fact that the standards regulating NO<sub>x</sub> emissions from stationary sources have been, and are expected to continue to be made more stringent.

**1.1.B. Chlorinated hydrocarbon wastes:** A recent DOE study [8] has identified chlorinated hydrocarbons (CHCs) as one of the most commonly reported contaminants in soils and groundwaters surrounding its facilities, with concentrations of some of these CHC species exceeding existing regulatory guidelines by as much as 10<sup>5</sup>. Among the technologies currently being considered for remediating large quantities of CHCs, heterogeneous catalytic oxidation processes and incineration are thought to be most effective at the present time [4c,9]. However, incineration in all likelihood will be a politically unacceptable technology [10] particularly for the mixed waste encountered in many DOE facilities, indicating an immediate need to actively pursue development of alternative catalytic processes. A number of recent reports in the patent literature and elsewhere describe new and promising catalytic materials and processes for the destruction of CHCs [4c,11]. Because these are very much developmental in scope at the present time, there are a number of technological hurdles to overcome, many involving the need for improved catalytic materials, before catalytic oxidation is a viable alternative for remediating large quantities of CHC wastes.

**1.1.C. Oxide-catalyzed petroleum refining:** Catalytic reforming is the second most important process for converting hydrocarbons in petroleum refining after catalytic cracking. Alkylation and transalkylation of aromatic compounds are also processes well known for their ability to produce products such as ethylbenzene, cumene, and linear alkylbenzenes, that are, in turn, important chemical precursors in the production of detergents and polymers. There has been recent renewed

interest in replacing the conventional catalysts for these processes, sulfuric acid, phosphoric acid, hydrofluoric acid, and aluminum chloride, with novel oxide 'superacidic' catalysts because the former materials typically produce undesirable by-products such as oligomers and heavy polyaromatic compounds, as well as an extremely corrosive sludge by-product [2,12,13].

## **1.2. The Importance and Difficulty of Studying Oxide Surface Chemistry:**

The three catalytic processes used as examples above have at least one important thing in common: they all currently use catalysts composed of oxide materials as in the case of SCR of NO<sub>x</sub> [2,3,4c], or oxide catalysts are being developed for their use [2,4c,11-13]. Besides these, transition metal oxides have found numerous applications as heterogeneous catalysts for other industrially important processes such as the selective oxidation, isomerization and metathesis of hydrocarbons [2,14,15]. In spite of their importance, oxide catalytic materials and processes have received much less attention from a fundamental science point of view than have catalysis by metals [2,14-18]. This is particularly so for the use of sophisticated ultra-high vacuum (UHV) techniques to characterize the surface properties of oxide catalysts even though the recent NRC [1] and DOE [2] reports discuss at length the usefulness of such tools for determining critical information about catalyst composition and structure. UHV techniques have only recently begun to be utilized to study the structure and surface chemistry of oxide materials [16] owing, in large part, to the difficulty of experimentally applying such tools to insulating materials, not to mention the inherent complexity and diversity of possible surface structures on oxides [16,19].

## **1.3. Catalysis Studies in the EMSL at PNNL:**

The work to be described here is taking place in the EMSL [20], a new DOE collaborative research facility at PNNL. The primary mission of the EMSL is to develop, refine, and use state-of-the-art research methods for investigating the molecular processes that underlie and control complex environmental processes. Four decades of production, testing, and operation of DOE nuclear weapons facilities has resulted in the interim storage of millions of gallons of highly contaminated radioactive, flammable and toxic wastes in hundreds of underground tanks, extensive contamination of the soil and ground water at thousands of sites within the U.S., and hundreds of buildings that must be decontaminated and decommissioned. The research in the EMSL is specifically focussed on DOE needs to cleanup and restore these sites. As indicated above, it can be expected that catalytic processes will play a major role in the cleanup of DOE sites, and that oxide-catalyzed reactions are likely to be particularly important. Therefore, we have initiated EMSL research programs that are performing molecular-level studies of oxide-catalyzed reactions and we describe some of these in this paper.

## II. EXPERIMENTAL

### II.1. Synthesis of Model Oxide Surfaces:

As noted above, UHV spectroscopic techniques are well established for the study of metal and semiconductor surfaces, materials that are readily available as bulk single crystals. Oxides, on the other hand, have been much less studied by these techniques because they are insulators and hence, susceptible to surface charging [16,18,19]. In addition, many of the oxides of catalytic interest are not generally available as macroscopic single crystals of suitable size. Those that are available typically possess a plethora of surface defects from polishing and cleaning processes, as well as bulk impurities which typically segregate to the surface during cleaning in UHV. However, it is possible to avoid these problems by employing the techniques of epitaxial growth. By growing thin ( $\approx 10$  nm), insulating films on conducting substrates [21-26], or by doping these epitaxial films to increase conductivity [27,28], it is now possible to obtain sufficient conductivity to perform these measurements. In addition, epitaxial growth techniques have enabled crystalline materials to be synthesized in thin-film form with a level of structural quality and purity that is unprecedented in bulk crystal growth technology [29]. We are using plasma-assisted molecular beam epitaxy (MBE) techniques to grow oxide thin-films to use as model catalyst substrates.

### II.2. Kinetic Studies of Model Catalysts:

We have constructed an apparatus that is capable of measuring reaction rates (using GC detection) under realistic, high-pressure ( $\sim 1$  atm.) conditions over these model, low surface area catalyst materials [30]. Details about studies of model catalysts with a combined catalytic reactor/UHV surface analysis apparatus are contained in a number of other places [1,2,31-33]. While such an approach has demonstrated utility for studying the catalytic chemistry of metal surfaces as described in some examples in the results section below, it has, at most, been used only a few times to address the catalytic behavior of oxide materials [34]. As with microreactor studies of realistic materials, reaction rates as a function of temperature and varying reagent partial pressures can be measured in this apparatus. From such data, a reaction mechanism can be proposed and a phenomenological kinetic model developed. In a few cases recently, high-pressure catalytic reaction rate data were successfully modeled using almost solely kinetic data for the elementary steps of the mechanism (*e.g.*, adsorption/desorption energetics) obtained in UHV measurements as parameters for the model [33,35]. In this way, a reaction mechanism is much more firmly established.

### II.3. UHV Studies of Oxide Surface Structure, and Chemistry:

Model studies such as those just described are extremely useful for inferring the identity of the catalytically active site(s) and of the various reaction intermediates, as well as in determining the overall rate of the catalytic process. This experimental information,

when coupled with experienced chemical intuition, can provide invaluable clues to the underlying elementary processes involved in the catalytic reaction. These processes include reagent adsorption onto, diffusion to and reaction at the active site(s), and, ultimately, product desorption from the catalyst surface. Unfortunately, the microscopic details of the dynamics and energetics associated with these elementary steps are not provided by the microreactor measurements on the model catalysts. Detailed information regarding the geometric and electronic structure of reactive surface sites, and adsorbed reagent, intermediate and product species is similarly absent. This type of information can be usefully determined by a number of UHV spectroscopic tools. In the present work, we are utilizing low-energy electron diffraction (LEED), X-ray photoelectron diffraction (XPD), vibrational (high-resolution electron energy loss, HREELS, and FTIR) spectroscopies, and scanning tunneling/force microscopies (STM/AFM) to determine the geometric structure of the substrate, and the adsorbate/surface complex formed by the chemisorption and surface reactions of the reactant molecules. Similarly, the electronic structure of the active surface site(s) and adsorbed species is being determined using XPS, ultraviolet photoelectron (UPS), and EELS spectroscopies. Temperature-programmed desorption (TPD) experiments are being used to determine surface coverages, reaction processes, and binding energies of adsorbed species.

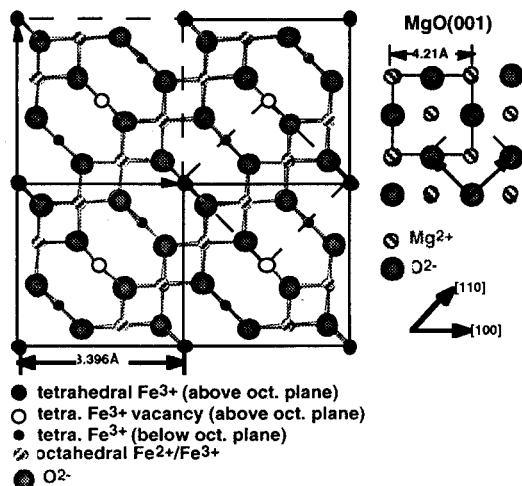
## III. RESULTS AND DISCUSSION

In this section, we will briefly present some examples from our recent work that will demonstrate how we are using the above-described experimental approach to address a number of critical aspects of the surface chemistry and catalytic properties of transition metal oxides.

### III.1. Synthesis of Model Oxide Surfaces:

We have used plasma-assisted MBE to synthesize a number of oxide thin films including MgO, TiO<sub>2</sub> (pure and Nb-doped), and the oxides of Fe [21-24,26-28], and have used them to study oxide surface structure and reactivity. Here we briefly give an example of this for the case of Fe<sub>3</sub>O<sub>4</sub>(001) grown on an MgO(001) surface (more details are contained elsewhere [26]). This substrate was chosen because of good lattice and crystal symmetry matching. The Fe<sub>3</sub>O<sub>4</sub>(001) film must be grown at a relatively low substrate temperature of 250 °C to avoid interface reaction and Mg outdiffusion. The surface was found to display a  $(\sqrt{2}\times\sqrt{2})R45^\circ$  reconstruction. A model proposed to explain the observed diffraction pattern, illustrated in Figure 1, consists of a tetrahedrally coordinated Fe<sup>+3</sup>-atom terminated surface with every other tetrahedral iron missing. These sites reside above a plane of iron (in octahedral coordination) and oxygen atoms where every other iron atom is in either a +2 or +3 oxidation state. Thus, this surface can be expected to display a rich

surface chemistry. We will discuss one example of this in the next section.



**Figure 1:** Proposed surface structure of  $\text{Fe}_3\text{O}_4/\text{MgO}(001)-(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ , along with the known surface structure of  $\text{MgO}(001)$  [26].

### III.2. UHV Studies of Oxide Surface Structure and Chemistry:

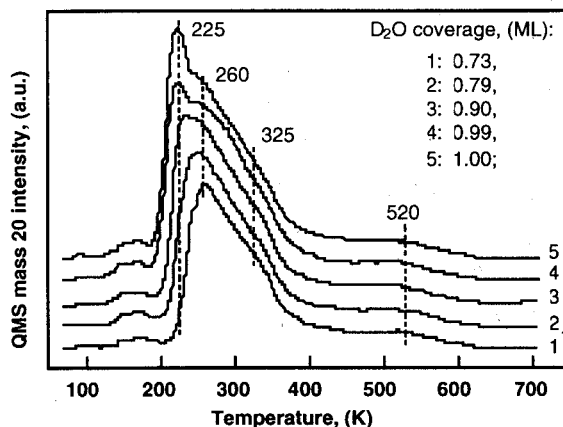
We have recently been studying the adsorption and reaction of water and formic acid on a number of single crystal [36-40] and model thin oxide films [21,24,41] and have found that the surface chemistry of these species is strongly dependent on the atomic-level structure of the oxide surface. For example, the dissociation of water to hydroxyl groups on  $\text{TiO}_2$  appears to require not only acidic cation adsorption sites, but also the close proximity of basic oxygen atoms in order for water O-H bonds to break [39]. Similarly, TPD results obtained on the reconstructed  $\text{Fe}_3\text{O}_4(001)$  described above, shown in Figure 2, contained three main chemisorbed states of water in the first monolayer, with TPD peak temperatures at saturation of 320, 280 and 225K, respectively [41]. We also found that each state is approximately equally populated with concentrations of around 1/3 ML. Recall from above that the proposed surface structural model, consistent with LEED results, consists of three distinct cationic iron sites, tetrahedral  $\text{Fe}^{+3}$ , and octahedral  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  sites, with approximately equal concentrations. For this reason, we have tentatively assigned the three TPD states to desorption of water from these three distinct iron-atom sites on the surface [41].

Further identification of the adsorption sites responsible for each TPD state was obtained by adsorbing water subsequent to oxidation of the surface. Oxidation was carried out by heating the sample to 350K during water exposure, resulting in a surface with a stoichiometry closer to  $\text{Fe}_2\text{O}_3$ ; i.e., only  $\text{Fe}^{+3}$  sites in the surface region. TPD of water from this “fully oxidized” iron oxide surface showed only the high and low temperature peaks at 320 and

225K, respectively [41]. Thus, it seems reasonable to assign the TPD peak at 280K to the desorption of water from octahedral  $\text{Fe}^{+2}$  sites on the  $\text{Fe}_3\text{O}_4(001)$  surface.

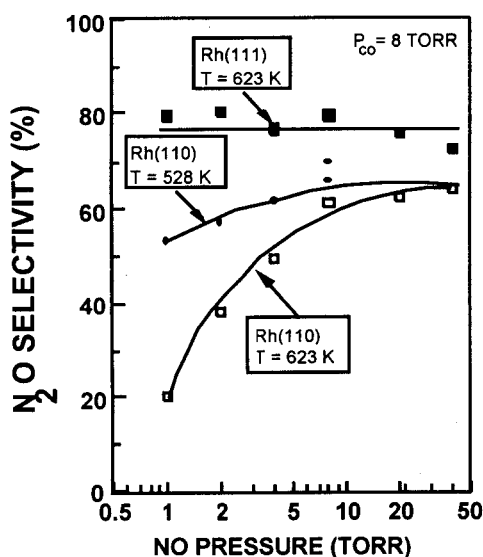
### III.3. Kinetic Studies of Model Catalysts:

The use of custom high-pressure catalytic reactor/UHV surface analysis instrumentation has provided significant new insights into the mechanisms of a number of metal-catalyzed reactions [30-33,35]. (Some recent examples of this from our work will be briefly described in the following sections.) However, we are aware of only two small recent efforts to apply such an apparatus to the study of the catalytic chemistry of oxide materials [34]. This is surprising considering its demonstrated utility to study metal-catalyzed reactions that are sensitive to surface structure [31,32,35]. The fact that the electronic structure of covalent and ionic insulators is highly localized in comparison with conductive metals, one might expect that oxide catalytic chemistry would be rich with examples of structure sensitivity [14,15,19]. Correspondingly, metal oxides can be expected to show a much greater diversity of surface structures including varied defect types and geometries so that it will likely be more difficult to define structure/activity relationships in these systems. For these reasons, we have recently initiated studies of a photocatalyzed oxidation of small hydrocarbon molecules over model single crystal titania catalysts, using our catalytic reactor/UHV surface analysis system. The results to date are too preliminary in nature for this paper. Rather, in the following we present some recent results from our studies of Rh-catalyzed  $\text{NO}_x$  reduction to demonstrate the types of useful information that can be obtained in these experiments.



**Figure 2:** Water desorption from a  $\text{Fe}_3\text{O}_4/\text{MgO}(001)-(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$  surface at water coverages near one monolayer (ML). Adsorption was carried out below 100K and the sample temperature was ramped at a rate of 2K/sec. From Reference 41.

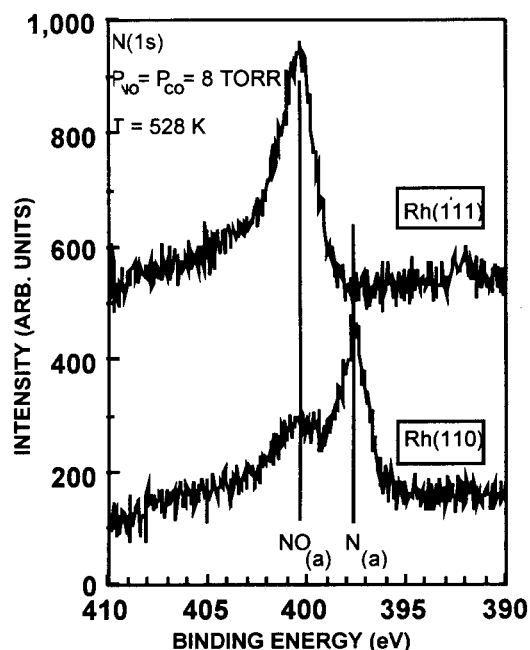
**III.3.A. Structure sensitivity in Oxide-Catalyzed Reactions:** The advantage of the catalytic reactor/UHV surface analysis apparatus is realized by the use of model catalysts, preferably single-crystalline in nature, that have a well-defined surface structure. On these model materials, the nature of the active site can be inferred and the relative activity of different sites assessed. This approach is particularly useful for addressing the origin of structure sensitivity in catalytic reactions [31,32,35]. For example, Figure 3 shows a recent measurement [32c] of the selectivity of the NO-CO reaction over two single crystal Rh surfaces. In this study, we found that the selectivity of two single crystal Rh surfaces displayed dramatically different selectivities for the two nitrogen containing products of the reaction,  $N_2$  and  $N_2O$ , with the (110) Rh surface favoring production of the desired product,  $N_2$ , relative to the (111) surface under all reaction conditions studied.



**Figure 3:** Selectivity for the undesirable product,  $N_2O$ , (relative to the total  $N_2$  and  $N_2O$  production) of the NO-CO reaction as a function of NO conversion over single crystal Rh(111) and Rh(110) catalysts. From Reference 32c.

**III.3.B. In-situ and Post-Reaction Surface Analysis:** Our catalytic reactor/UHV surface analysis apparatus also has capabilities for *in-situ* fourier transform infrared (FTIR) spectroscopy that can be used to identify both adsorbed and gas-phase chemical species present during reaction [42]. The presence or absence of various proposed reaction intermediates can be readily determined from the *in-situ* spectra [30,42]. The high-pressure reactor is directly coupled to an ultra-high vacuum (UHV) chamber that houses a variety of surface

analytical probes, including Auger electron (AES) and x-ray photoelectron (XPS) spectroscopies, low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD). These various *in-situ* and *ex-situ* spectroscopies provide a fairly complete picture of the chemical state of the active catalyst surface. Notably, they provide information about the concentration of reaction intermediates, the oxidation state(s) of the constituents of the catalyst surface, and the structure of the active surface sites. Again using our recent studies of the NO-CO reaction over Rh single crystal surfaces [32c] as an example, Figure 4 shows XPS data obtained after high pressure reaction over Rh(111) and Rh(110). In the figure, it can be seen that reaction on the surface was found to be most selective for  $N_2$ , Rh(110), takes place at much higher steady-state concentrations of adsorbed N-atoms than does reaction on Rh(111).



**Figure 4:** N(1s) XPS spectra obtained after NO-CO reaction ( $P_{NO} = P_{CO} = 8$  Torr;  $T = 528$ K) on Rh(111) and Rh(110) single crystal catalysts. After high temperature reaction, the sample is cooled in the gas mixture, reaction rate measurements made, gases pumped from the reactor, and samples introduced into the UHV chamber for XPS analysis. From Reference 32c.

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- [6] Consider that concentrations of nitrite and nitrate species in Hanford tank wastes are estimated to be about  $1.1 \times 10^8$  kg, in addition to about  $5.4 \times 10^7$  kg present in contaminated soils [5b]. Currently, all tank wastes are scheduled to be sent to vitrification plants for final storage in waste-glass "logs". However, there are two major problems with this plan that are associated with the large quantities of nitrite and nitrate wastes; namely that 1) vitrification of all of the tank waste will be prohibitively expensive (current estimates suggest that about 40,000-60,000 glass "logs" will be required and each "log" is estimated to cost about \$0.5 million to manufacture and an additional \$0.5 million to transport and store in a permanent repository), and 2) large concentrations of nitrite and nitrate species are incompatible with the current baseline waste-glass materials. For this reason, it is likely to be necessary that these species be removed from the waste stream prior to sending the feed to the vitrification plant(s). Unfortunately, current methods for denitrification of aqueous solutions result in the conversion of dissolved nitrite and nitrate anions into gaseous  $\text{NO}_x$ . (Even if a pretreatment for nitrate and nitrite destruction is not performed, exposure of the feed to the high temperatures of the glass melters will likely cause much of the nitrate and nitrite waste to be converted to gaseous  $\text{NO}_x$ .) Current U.S. and Washington state regulations effectively limit gaseous  $\text{NO}_x$  emissions to about 40 tons (or  $3.6 \times 10^4$  kg) per year for any new "stationary source" on the Hanford site [7]. (Note that these regulations have become and are expected to continue to be more stringent over time.) With an expected 20 year lifetime for the vitrification plant(s), less than 1% of the total nitrate and nitrite inventory can then be emitted as gaseous  $\text{NO}_x$ . This level of destruction (> 99%) is well above the capability of current technologies that only remove at best 90% of  $\text{NO}_x$  (for the case of catalytic SCR, 60-90% efficiencies are reported, while other technologies are even less efficient and produce secondary waste streams [3]). Note that these reported destruction efficiencies are for gaseous feeds with much lower concentrations of  $\text{NO}_x$  (ppm levels) than is expected to be encountered in gaseous emissions from Hanford processing plants so that 90% efficiency using current SCR technology is likely to be an overestimate by a significant amount. However if 90% destruction could be achieved, a total of about  $1 \times 10^7$  kg of  $\text{NO}_x$  would still be emitted. For this amount, over 300 years of emissions would be required to meet the present limitation of  $3.6 \times 10^4$  kg/year. While purification and recycle of the nitrite and nitrate might be desirable as an alternative, it is unlikely that such a material would be acceptable for applications off the Hanford site so that it will ultimately need to be stored as mixed waste and/or destroyed. Furthermore, efficiencies for these technologies are currently less than that for SCR [3].
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