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MOLTEN SALT OXIDATION OF MIXED WASTES: SEPARATION OF RADIOACTIVE MATERIALS AND RESOURCE CONSERVATION AND RECOVERY ACT (RCRA) MATERIALS*

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ABSTRACT

The Oak Ridge National Laboratory (ORNL) is participating in a program to apply a molten salt oxidation (MSO) process to treatment of mixed (radioactive and RCRA) wastes. The salt residues from the MSO treatment will require further separations or other processing to prepare them for final disposal. A bench-scale MSO apparatus is being installed at ORNL and will be operated on real Oak Ridge wastes. The treatment concepts to be tested and demonstrated on the salt residues from real wastes are described.

INTRODUCTION

The Oak Ridge National Laboratory (ORNL) is involved in a program to apply a molten salt oxidation (MSO) process to the treatment of mixed wastes at Oak Ridge and other Department of Energy (DOE) sites. Mixed wastes are defined as those wastes that contain both radioactive components, which are regulated by the atomic energy legislation, and hazardous waste components, which are regulated under the Resource Conservation and Recovery Act (RCRA). A major part of our ORNL program involves the development of separation technologies that are necessary for the complete treatment of mixed wastes. The residues from the MSO treatment of the mixed wastes must be processed further to separate the radioactive components, to concentrate and recycle residues, or to convert the residues into forms acceptable for final disposal. This paper is a review of the MSO requirements for separation technologies, the information now available, and the concepts for our development studies.

HISTORY OF MOLTEN SALT OXIDATION FOR WASTE TREATMENTS

Molten salt oxidation is not a new idea, having been initially introduced in the early 1950s by the Atomic Energy Commission (AEC) as a possible method of processing nuclear fuels. Rockwell International carried out AEC-sponsored basic research with molten salts. One of the first applied uses for molten salt examined by Rockwell was as a scrubber for SO_2 emissions from a coal gasification plant. It was this application that gave Rockwell the concept of using molten salts, specifically carbonates, to treat hazardous waste.

Rockwell has done tests on many hazardous compounds, such as polychlorinated biphenyls (PCBs), tributyl phosphate (TBP), and various chemical weapons (1,2). All tests showed excellent destruction efficiencies. Rockwell also performed test runs with simulated radioactive waste to show that radioactive particles would be retained in the salt (3). Even though these results showed effective treatment of wastes, incineration systems appeared to be more practical and more economical; most MSO research ended about 1982.

MSO has recently been brought back into the picture as a possible treatment for mixed waste. A recent test run performed at the Energy Technology Engineering Center (ETEC) on a hydrocarbon oil with low levels of ^{137}Cs and ^{60}Co showed promising results. The unit performing this test has been shipped to ORNL for further studies with DOE mixed wastes.

MSO PROCESS DESCRIPTION

The MSO process is fairly simple, as is illustrated in Figure 1. The salt is placed in either a metal or, more commonly, ceramic vessel. Generally, the height of the salt under static conditions should be roughly equal to the diameter of the vessel. The salt charge is preheated to the desired temperature (650—1100°C depending on the

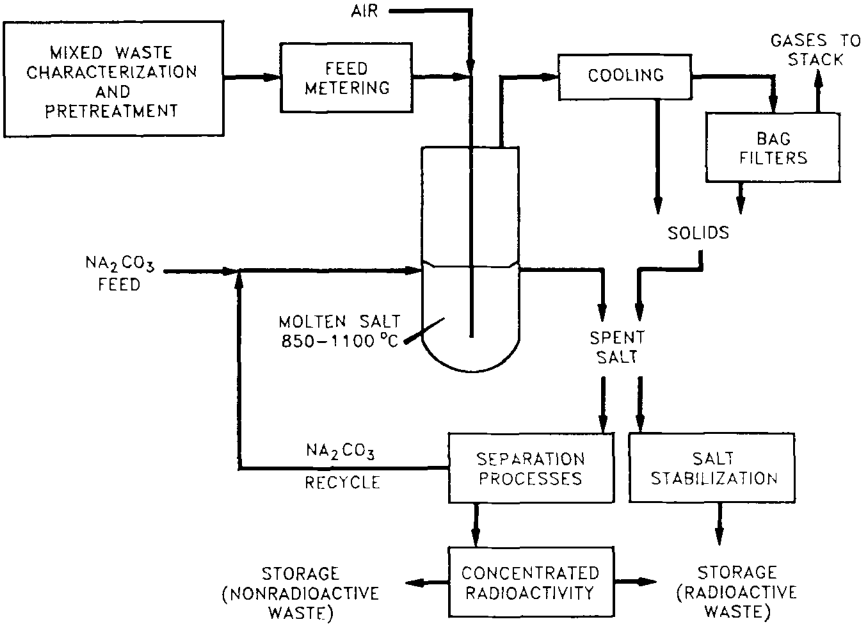

Fig. 1. Molten salt oxidation of mixed wastes and treatment of residues.

salt composition). The temperature must be high enough to reduce the salt's viscosity until it is similar to that of water. This allows for proper contact of air and feed with the salt bath. A Na_2CO_3 melt requires temperatures ≥900°C (melting point of 851°C) and probably a ceramic vessel. Metal alloy vessels might be used for salt mixtures with lower melting points.

The waste and air enter the salt either from the top of the vessel through an injection tube which ends about 2 in. from the base of the vessel, or they are fed through the vessel walls. The waste feed rate is limited by two conditions: (1) the exiting combustion gases should not have a superficial velocity >2.5 ft/s or else there may be excessive entrainment in the off-gas stream, and (2) the heat produced from the waste must not raise the salt's temperature. The off-gas is passed through a prefilter system and then through an absolute filter before it is released to the atmosphere. The salt composition is controlled by addition of Na_2CO_3 and removal of spent salt.

MOLTEN SALT OXIDATION FOR TREATMENT OF MIXED WASTES

For the purpose of describing the residues from treatment of mixed wastes, the MSO treatment involves simple chemical reactions. The waste, excess oxygen (or air), and the Na_2CO_3 are reacted to very nearly the chemical equilibrium at the molten salt temperature. The molten Na_2CO_3 reacts with acid gases to form sodium salts and CO_2. The Na_2CO_3 is reported to act as a catalyst. The destruction efficiencies for toxic organics are as good (high) in molten salt at 900 to 1000°C as for simple incineration at temperatures over 2000°C. Carbon and hydrogen are discharged as CO_2 and H_2O.

One important characteristic of MSO as a waste treatment is the good retention of metals as oxides or salts in the salt residues. The entrained or condensed solids in the cooled off-gases are easily collected and discharged as a residue by bag filters. Acid gases react with Na_2CO_3 in the melt and are retained as the sodium salts. The MSO treatment results in efficient destruction of waste constituents to yield salt residues and off-gases without any aqueous scrubber residues.

The efficient collection of metallic salts and ash in the salt residues is both an advantage and limitation for MSO treatment of mixed wastes. The MSO treatment is not suitable for high contents of ash or noncombustible solids in the waste feed; excessive amounts of the carbonate salt would be removed as residues in order to remove these solids. High concentrations of elements that form acid gases when reacted with oxygen (Cl, F, S, P, etc.) convert large amounts of Na_2CO_3 to the corresponding sodium salts. The same amounts of sodium salts are formed in the scrubbers for incinerators. Whether the salt residues or the scrubber slurries are preferred residues is not obvious.

A conversion of an unstable mixed waste form to a thermodynamic stable form is very important for environmental, safety and health (ES&H) reasons. A mixed waste treatment system must meet this requirement, and there will be an additional advantage if the treatment system can produce a mixed waste product that has a smaller volume than that of the original treatment feed. The MSO treatment produces a dense, solid sodium carbonate base that is considerably easier to manage than the volatile liquid mixed waste or the combustible solid mixed waste. This conversion is a definite advantage for mixed waste management, but the additional volume reduction will also be realized for many mixed wastes. Table 1 gives the calculated volume reduction

TABLE 1. MIXED WASTE VOLUME REDUCTION RATIOS

Waste Description	Location	VRR	Limiting Factor
Oil/Solvent	RF	70	Ash[a]
LBL Scintillation Fluid	LANL	60	Ash[a]
DWPF Benzene	SR	59	Ash[a,b]
Bettis Oil/MSF-008,010	OR	58	Ash[a]
Decontamination Solvent	INEL	16	NaCl, NaF
ORNL Waste Oil	OR	9.3	NaCl, Na_3PO_4
TRU Graphite	INEL	7.3	Ash[a]
2/3 Oil — 1/5 Tetrachloroethane ($C_2H_2Cl_4$)	OR	2.6	NaCl, NaF
Trichloroheptafluorobutane	OR	0.44	NaCl, NaF[b]
Perfluorodimethylcyclohexan, E(C_8F_{16})	OR	0.36	NaFl[b]

[a] Assuming maximum ash content of waste.
[b] Radioactive isotope and RCRA metal content of waste is unknown.

ratios for several mixed waste that may be treated by MSO. The limiting conditions for these treatments are relative to the molten salt. The treatment extends to the point that the salt accumulates 20 vol % of ash, the sodium halide content is equal to the sodium carbonate content, or the contact radiation levels reach 20 mR.

FINAL WASTE FORM CONSIDERATIONS

Waste treatment processes commonly generate residues. A primary objective of the overall treatment is to have all residues in a form acceptable for final disposal. For mixed wastes, the disposal of residues is very dependent on whether the original waste feed was considered hazardous as a listed or a characteristic waste under RCRA. The MSO treatment of mixed wastes generally gives high destructions of hazardous organic compounds and can be operated to eliminate the original characteristic hazards of ignitibility, corrosivity, and reactivity. The eight metallic elements that result in a characteristic toxicity hazard (Ar, Ba, Cd, Cr, Pb, Hg, Se, and Ag) would remain (as oxides, salts, or metals) in the residues. Overall, if the mixed waste were characteristically hazardous under RCRA, the MSO residues could probably be nonhazardous and could, thus, be disposed of subject to the DOE guidelines for radioactive wastes.

The final disposal of residues is much more difficult if the original waste is a listed hazard under RCRA. Any residues from treatment of a listed waste are considered to also be listed wastes. While the radioactive constituents may be changed chemically by waste treatments, they remain radioactive. There is no approved final disposal for these mixed waste residues. Separation and concentration of the radioactivity can give a much smaller volume of mixed waste and a larger residue for disposal as a hazardous waste solid. In theory, a residue can be "delisted" if the feed composition to a treatment and the performance of the treatment process can be standardized and demonstrated. This is very difficult and is not practical for the varied compositions of most of the Oak Ridge DOE wastes.

In summary, the salt residues from MSO treatment of mixed wastes will require further separations or other processing to prepare them for final disposal. The radioactivity should be concentrated to a minimum volume. For mixed wastes that are hazardous by characteristics, the residues can probably be RCRA nonhazardous and then can be disposed of as radioactive solid wastes. For listed mixed wastes, the best result currently possible is a minimum volume of mixed waste with no approved disposal option. The acceptable final solid forms are likely to incorporate the residues into glass, hydraulic cements, ceramics, organic matrices, or sulfur polymer materials. For MSO waste treatment residues, both the processing into such solid forms and the performance of such forms remain to be demonstrated.

APPLICATIONS OF MSO TO DOE OAK RIDGE MIXED WASTES

The Chemical Development Section (CDS) of the Chemical Technology Division at ORNL has received a prototype MSO unit from ETEC. It has been brought to ORNL for the primary purpose of demonstrating the MSO treatment of real mixed wastes at the three Oak Ridge sites. Important information to be obtained from the MSO tests will be the destruction efficiency of organic compounds, the final location of radionuclides and RCRA materials, and the compatibility of materials. Operating procedures and test measurements will also be evaluated and modified as required.

The unit from ETEC is shown in Figure 2. In addition to what is depicted in the figure, it is worth noting that the off-gas is analyzed for CO_2, CO, NO_x, O_2, and hydrocarbons, which allow a comparison of the combustion products versus melt composition. The salt composition is analyzed from periodic samples of the melt. Unfortunately, a real-time measurement of salt composition has not yet been devised.

Prior to any tests in the MSO unit, the process will be modeled for that specific waste feed using readily available thermodynamic programs to predict system behavior. This will be done mostly as a safety feature to ensure compatibility of materials but will also provide a theoretical basis for comparison and analysis of results.

The variables that will be examined in the CDS study are waste composition (chemical and physical), salt composition, temperature of the salt bath, waste feed rate, and percent excess air. Waste composition is obviously the most critical variable, causing the others to be modified to give the best results (i.e., greatest organic destruction and retention of radioactive and RCRA materials in the melt). The general order of testing at ORNL will be as follows:

1. Pure hydrocarbons,
2. Halogenated hydrocarbons,
3. Hydrocarbons containing nitrate groups,
4. Halogenated hydrocarbons containing depleted uranium,
5. Halogenated hydrocarbons containing fission products,
6. Organic sludges,
7. Activated carbon, and
8. Organics containing beryllium.

The first three tests will be primarily concerned with off-gas release as a function of the above-mentioned variables. They will also provide operating experience with the unit before radionuclides are introduced. The next two tests will concentrate on entrainment and volatility of radionuclides. Tests 6 and 7 will focus on feeding mechanisms and reaction rates for solid-containing components. The final test is being considered because beryllium is presently a problem for incinerators due to the toxicity of BeO.

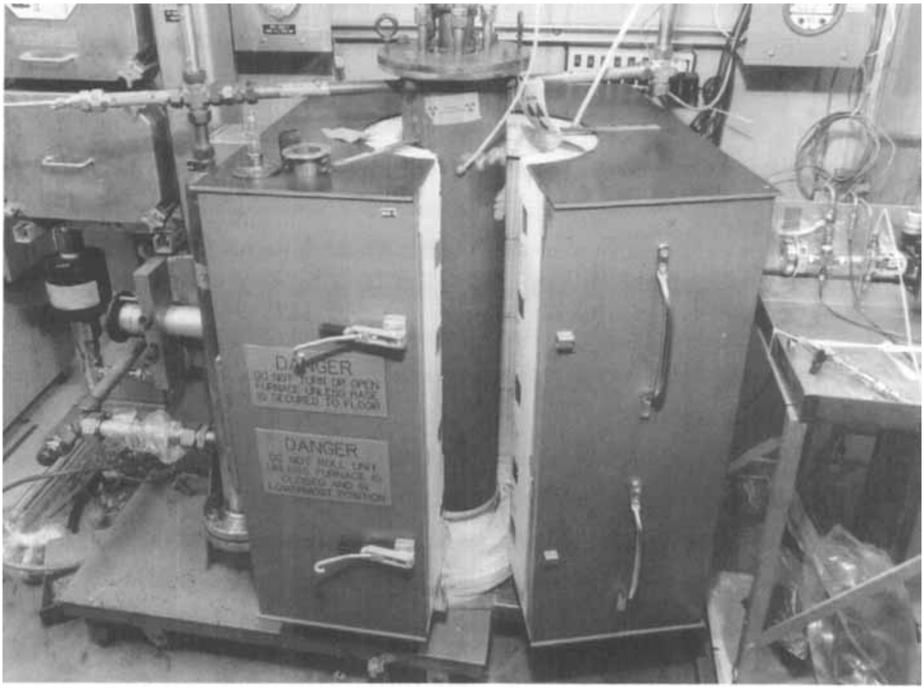

Fig. 2. Bench-scale Molten Salt Oxidation system at ORNL.

These tests will (1) demonstrate which waste and which conditions allow effective treatments and (2) determine the optimal operating conditions.

Along with the prototype MSO treatment of mixed waste, Oak Ridge has proposed a pilot plant scale MSO for treatment of Oak Ridge mixed waste. Some technical concerns for a MSO pilot plant and answers are presented below. The nine concerns are listed just as they were received, and the response follows:

1. **Safety questions on Pu and certain other radionuclides volatility. Can MSO equipment qualify for radioactive operations?**

   Radionuclide volatilities are major interest to the MSO. Some of the radionuclides may have observable volatilities in the MSO operations. The first management practice is to reduce these volatilities by chemical additions, and the second is the use of absolute filters in the off-gas system.

The MSO can qualify for radioactive operations. A larger, similar technology is being tested for reprocessing LMFBR fuels at the Idaho site. The IFR development program has a large hot cell equipped with molten salt technology equipment for processing 100 kg of spent LMFBR fuel per day.

On the other hand, the proposed pilot-scale MSO operations at Oak Ridge will not address Pu wastes. This proposed system will deal with the magnitudes of DOE low-level mixed waste. The actual spent salt product can be limited to class "C" levels of radioactivity, but a more useful and safe system could operate with salt levels at 20 mR/h.

2. **Safety questions about the steam explosions.**

   Steam explosions occur when large volumes of water are quickly heated. The input stream of the MSO usually will not include aqueous solutions. Mixed wastes with portions of water when injected into the MSO will not include sufficient water for a steam explosion. The small portion of water will be quickly volatilized to small quantities of steam. The high temperature, the low water input, and the system throughput will prevent the conditions for steam explosion. In the event of an aqueous solution feed, that feed will be admitted to the MSO at a rate such that steam explosion cannot occur.

3. **Severe corrosion of the MSO reactor vessel by the salt and halide contaminants. Potential to create secondary waste from discarded MSO units.**

   The MSO reactor vessel is a ceramic material, alumina, which is very corrosion resistant to the salt bed and the chloride, bromide, or iodide contaminants. The vessel operating lifetime of ~ 3000 hours is anticipated for an operation at 900°C with halide waste components. An equipment change in the low-level radiation environment will not be a major event. Fluoride concentrations greater than 10% and at 1000°C will be corrosive to alumina, but administrative control can prevent this.

   There is also the probability that a special version of stainless steel or high nickel alloys will better accommodate the MSO. If such materials become available, the reactor vessel can be changed from the ceramic to the steel component.

4. **Solid waste feed not developed.**

   Pilot-scale feed systems for flowable solids are commercially available and are in wide use in solid processing industries. Rockwell conducted a successful large-scale solids feed development program in the 1970s for low-level RA solid wastes for INEL. Laboratory-scale solid feed systems are not commercially available and must be designed and built. There is not single generic solid feed system, since different types of solids have different feeding properties.

However, several solid feed technologies for MSO have been considered: (1) a dry solid that can be ground into small particles can be fed as part of the gas input streams; (2) extrudable materials can be extruded into a rod form that can be controlled fed into the melt; and (3) wet (aqueous or organic) solids can be ground and fed as a slurry. These three techniques can handle most solids and these feed streams can be supplied to the melt through the top portion of the vessel.

5. **Inorganic constituents to increase the viscosity of the molten salt bed to a point where it may solidify.**

This could occur if the inorganic constituents consist of ash-like inert materials. However, even in this case, the salt would be removed when its viscosity reached a comfortable engineering limit — long before the melt would solidify. At any rate, MSO is not recommended for materials that have high ash content.

Ash content from an oxidation technology is a function of incomplete oxidation and non-oxidizable components. Since the MSO supplies maximum oxidation compared to other technologies, the expected ash content for a given feed material will be minimized. Current MSO efforts will consider development of procedures for monitoring the salt viscosity.

6. **Dispersion of finely divided gas bubbles through the viscous salt bed and unknown impact of mass transfer of the pollutants of concern to the carbonate bed.**

As stated in the answer to question 5, we avoid wastes that have a high ash content, which would lead to an excessively high viscosity. If treating such a waste is necessary, the salt is replaced when the viscosity becomes high. Many wastes will be treated without a significant increase in the salt viscosity. The MSO will not be operated when the contact between wastes and molten salt is inadequate.

7. **CO emissions for chlorinated waste are about 10,000 ppm.**

CO emissions are a function of salt composition, temperature, waste composition, and oxidation potential. CO emissions are very low when the $CaO\text{-}CaC_2$ *system is used. However, even with the* Na_2CO_3 *system, the problem can be easily corrected by incorporating an off-the-shelf catalyst for converting the CO to* CO_2 *emissions. Variables that can be tested are melt temperature, feed droplet size, melt additives, and/or* O_2 *concentration. The CO emissions are controllable.*

8. **Methods for the final waste form not developed and recycling of the salt.**

There is no approved final waste form for any radioactive waste management system. Even the Savannah River Vitrification Plant plans to produce glass logs *without an available repository. Low-level waste forms as grout/cement are used for special management projects with close surveillance by compliance groups. Also, the New Mexico WIPP has not decided if they will receive processed wastes, and is far from deciding if they will receive remote-handled TRU waste. Therefore, not having a final waste form is a general problem for waste management processing.*

9. **Methods for the final waste form not developed.**

The original pilot plant for mixed waste can be operated for a couple of years where the activity of the salt does not exceed class "C" level waste. In this time frame, the success of MSO for mixed waste treatment will be established. This class "C" sodium carbonate is very amenable to the well-known grout or cement waste form.

Rockwell has some preliminary results that suggest that the radioactivity of the melt can be removed and concentrated and the salt can be considered for recycle. This spent salt technology will be examined in the next two years, and a spent salt processing unit can be added to the pilot plant.

Perhaps the only way for DOE to have a mixed waste processing system is to build a pilot plant to perform and probe a treatment system before a final waste form is developed. However, the proposed pilot plant must have good suggestions for the final waste forms. The MSO pilot plant does include a management plan for the resulting radioactive waste; first, operate the system so that the spent salt fits into a solid low-level waste form, and second, develop a spent salt recycle plan to separate and minimize the radioactivity.

The treatment of many mixed waste forms will leave the radioactive residues in the spent salt. However, there will be mixed waste forms that have RCRA metals and LLW radioactive components in the salt. Management of this low volume RCRA spent salt will also need development. The conversion of this salt into a nonleachable form must consider the EPA leach rate conditions, as well as the radioactive leach rate conditions.

SEPARATIONS AND TREATMENTS FOR SPENT SALT

The salt products from a molten salt oxidation of mixed wastes will be treated to meet the requirements for one of three dispositions: a recycle of Na_2CO_3 (with small amounts of other salts and/or radioactivity) to the molten salt oxidation; disposal as a nonradioactive waste; or long-term storage as a radioactive waste. All the spent salt could be stabilized in some way and stored as radioactive waste without use of any separation processes (Figure 1). It is probably economically desirable to minimize the storage costs by separating either Na_2CO_3 for recycle or a nonradioactive waste salt to give a smaller volume of more concentrated radioactive waste.

The spent salt discharged from an MSO treatment of wastes will have varying compositions of Na_2CO_3, other sodium salts, radioactivity, and ash or other solids. The solids removed from the cooled off-gas are likely to be low in Na_2CO_3 and high in more volatile compounds such as NaCl, CsCl, or phosphorus oxides. The salt removed to avoid excessive depletion of Na_2CO_3 as a chemical reagent is also likely to be low in Na_2CO_3. The Na_2CO_3 recycle would do little to reduce the total waste volume for these compositions. When salt is replaced to control the physical properties of the melt (<20 wt % solids to prevent excessive viscosities or a limit on NaCl concentration to limit the vapor pressure), then Na_2CO_3 recycle may be important to reduce the volumes of wastes.

An aqueous dissolution of spent salt and separations of the components have been proposed (3), and some experimental results are reported (4). The ash or insoluble metal oxides are filtered from the solution. Evaporation and crystallization at two different temperatures can separate Na_2CO_3 (containing some NaCl, Na_2SO_4, and other sodium salts) for recycle and NaCl for disposal. The radioactive components are generally a very small mass fraction of the spent salt. Separation of the insolubles and some ion exchange separations can give a small mass of radioactive waste and much larger amounts of decontaminated waste. The dissolved spent salt is a caustic solution of high sodium concentration. This is chemically very similar to the supernates in many DOE tank wastes. Therefore, the separation technology developed for removal of radionuclides from these tank supernates should work well for the dissolved spent salts. The recent experimental results for an MSO test with waste oils demonstrated good decontamination of dissolved salts by removal of cesium (4).

A recycle concept proposed for study at ORNL is a molten salt extraction of NaCl and fission products with recycle of the Na_2CO_3 and other unextracted components (5). The concept is a solvent extraction separation with two immiscible salts. Selective extractions of actinides and fission products have been reported for some immiscible chloride salts. If laboratory studies can identify an immiscible second salt and significant separation factors for the MSO waste salt components, then a complete separation scheme might be possible. An auxiliary concept is an electrolysis to remove Cl_2 and recycle Na_2O or Na_2CO_3 to the MSO process.

Concepts for stabilization of spent salts for storage have been proposed. Formation of glasses and leach tests were reported for 10 to 40 wt % salts (NaCl and Na_2SO_4) (2). Cementation of 10 to 40 wt % salts (Na_2CO_3-Na_2SO_4-NaCl) gave cements with leach rates about 10 times greater than the glasses. These old results could not meet the current waste leach specifications, but the technology for both glasses and cementation has been greatly improved.

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