DEWATERING OF CONTAMINATED RIVER SEDIMENTS

Ronald H. Church
U.S. Bureau of Mines
Tuscaloosa Research Center
P.O. Box L, Univ. of Alabama Campus
Tuscaloosa, AL 35486-9777

Carl W. Smith
U.S. Bureau of Mines
Tuscaloosa Research Center
P.O. Box L, Univ. of Alabama Campus
Tuscaloosa, AL 35486-9777

Bernard J. Scheiner
U.S. Bureau of Mines
Tuscaloosa Research Center
P.O. Box L, Univ. of Alabama Campus
Tuscaloosa, AL 35486-9777

ABSTRACT

Dewatering of slurries has been successfully accomplished by the proper use of polymers in flocculating the fine particulate matter suspended in mineral processing streams. The U.S. Bureau of Mines (USBM) entered into a cooperative research effort with the U.S. Army Corps of Engineers (Corps) for the purpose of testing and demonstrating the applicability of mining flocculation technology to dredging activities associated with the removal of sediments from navigable waterways. The Corps has the responsibility for maintaining the navigable waterways in the United States. Current technology relies primarily on dredging operations which excavate the material from the bottom of waterways. The Corps is testing new dredging technology which may reduce resuspension of sediments by the dredging operation. Pilot plant dredging equipment was tested by the Corps which generated larger quantities of water when compared to conventional equipment, such as the clam shell. The transportation of this "excess" water adds to the cost of sediment removal.

The process developed by the USBM consists of feed material from the barge being pumped through a 4-in line by a centrifugal pump and exiting through a 4-in PVC delivery system. A 1,000-gal fiberglass tank was used to mix the polymer concentrate. The polymer was pumped through a 1-in line using a variable speed progressive cavity pump and introduced to the 4-in feed line prior to passing through a 6-in by 2-ft static mixer. The polymer/feed slurry travels to the clarifying tank where the flocculated material settled to the bottom and allowed "clean" water to exit the overflow.

A pilot scale flocculation unit was operated on-site at the Corps' "Confined Disposal Facility" in Buffalo, NY. A loaded barge containing sediments dredged from the Buffalo River was delivered to the disposal facility for the flocculation studies. Contaminated sediments were pumped from the barge to the flocculation unit. Tests were conducted using polymer concentrations of 0.01, 0.02, 0.03 pct, pumped at variable flow rates. Feed slurry from the barge consisting of approximately 1.5 pct solids was pumped through the unit at approximately 230 gal/min. The Nephelometric Turbidity Units (NTU) values (which measures the turbidity of the water by measuring the light scattered at 90° or 270° through the incident beam) of the discharge water ranged from 12 to 17 with the underflow discharge containing approximately 31 pct solids. This would require only one barge (at 31 pct solids) instead of 20 (at 1.5 pct solids) to deliver the same quantity of contaminated river sediments.

Costs associated with the polymer requirements were calculated from the original costs of the polymer when purchased in bulk ($0.50 per lb). Treatment of 1,000 gal of 1.5 pct contaminated river sediments requires less than $0.01 of polymer (less than $10.00 per 5,000 cubic yard barge).

BACKGROUND

The 1987 amendments to the Clean Water Act authorized U.S. Environmental Protection Agency's (EPA) Great Lakes National Program Office (GLNPO) to coordinate and conduct a 5-year study and demonstration project on the treatment of toxic pollutants in bottom sediments. Five priority areas were selected for demonstration projects: Saginaw Bay, MI; Sheboygan Harbor, WI; Grand Calumet River, IN; Ashtabula River, OH; and Buffalo River, NY.

In response, GLNPO launched the Assessment and Remediation of Contaminated Sediments (ARCS) program. (In November 1990, the Great Lakes Critical Programs Act was passed, extending ARCS by one year, until December 1993.) ARCS is an integrated program for developing and testing assessment and cleanup alternatives for contaminated sediments. Information from the ARCS program will be used to guide the development of Lakewide Management Plans and remedial action (cleanup) plans for the 43 Great Lakes "Areas of Concern" identified by the U.S. and Canadian governments.

GLNPO is responsible for administering the ARCS program, but it is a joint effort. Other participants in ARCS are EPA headquarters and EPA Regions 2, 3,and 5; U.S. Fish and Wildlife Service; National Oceanic and Atmospheric Administration; Bureau of Mines; Great Lakes State agencies; and many universities and public-interest groups (1).

As part of this program, the Bureau of Mines entered into a cooperative research effort with the U.S. Army Corps of Engineers for the purpose of testing the applicability of mining technology in clean-up activities associated with contaminated river sediments. Over many years, pollution of the rivers has resulted in concentrated toxins being deposited in the river bottom sediments. Current technology relies primarily on dredging operations which "digs" the material from the bottom; which in turn, can reintroduce the toxins into the waterways.

As part of the ARCS program, the Corps of Engineers is testing new technology which may help eliminate the reintroduction of toxins. Pilot plant dredging equipment was tested which generated larger quantities of water than the current technology employed. The transportation of this "excess" water adds to the cost of sediment removal.

The USBM's contribution in this effort has been the development of low cost methods to flocculate the particulates which would allow the "clean" water to be directly returned to its source, i.e., the river, reducing costs by eliminating the transportation, handling, and disposal of excess water in the CDF (confined disposal facility). Also, techniques such as flocculation result in higher percent solids of dredged material in the CDF and could therefore increase the capacity of the CDF. The technology tested was pioneered by USBM in the dewatering research activities associated with mineral recovery, waste minimization, and waste utilization at mining operations (2).

TECHNOLOGY EMPLOYED

Dewatering of slurries has been successfully accomplished by the proper use of polymers in flocculating the fine particulate matter suspended in mineral processing streams. The adsorption of polymers on particulates is dependent upon the type, molecular weight, and concentration of functional groups associated with the polymer, as well as the surface charge, porosity, purity, and solution properties associated with the suspended particulates.

Three series of polymers (anionic, zero charge, and cationic) were lab tested on a sample of Buffalo River sediment obtained from the Corps. From these studies, a slightly anionic polymer (Photafloc 1110[1] manufactured by Neutron Products, Inc.) was selected for the field demonstration. This polymer sells for $0.50 to $0.75/lb depending upon the volume purchased. A 3.2-pct solution of this polymer was obtained from the manufacturer for the testing program described in this report.

POLYMER CHARACTERISTICS

Photafloc 1110 is an anionic copolymer of acrylamide and sodium acrylate with a molecular weight in excess of 10 million. It is a slightly basic, nonhazardous aqueous solution. The polymer solution contains a small amount (less than 0.02 pct) of unreacted acrylamide monomer, CAS 79-06-1, which has an OSHA-PEL (permissible exposure limit) of 0.03 mg/m^3.

The American Council of Governmental Hygienists recommends a TLV-TWA (threshold value limit; 8 hour time weighted average) of 0.03 mg/m^3 for skin exposure. This acrylamide monomer level will not normally be reached when handling the solution. Also present is a small amount of sodium acrylate. The polymer is not listed as a carcinogen by the NTP, nor is it regulated by OSHA. Also, it is not listed in Federal hazardous waste regulations (40 CFR 261.33, Paragraphs (e) and (f)), and does not exhibit any of the hazardous characteristics listed in 40 CFR 261, Subpart C.

SYSTEM DESIGN

Figure 1 is a drawing of the field test flow sheet used for the Buffalo River demonstration project. For this test, the feed material from the barge was pumped through approximately 200 ft of 4-in line to a 6-in diesel centrifugal pump necked down to a 4-in PVC delivery system. A 1,000-gal fiberglass tank was used to mix the polymer concentrate.
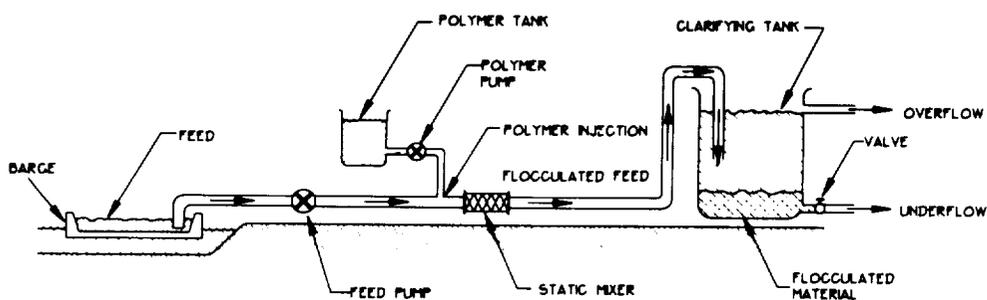

Figure 1. Flowsheet for the flocculation tests
conducted at the Buffalo River.

The polymer was pumped through a 1-in line using a variable speed moyno type pump and introduced to the 4-in feed line prior to passing through a 6-in by 2-ft static mixer. The polymer/feed slurry traveled approximately 270 ft to the clarifying tank (approximately 1,700 gal at the overflow) where the flocculated material settled to the bottom, and allowed "clean" water to exit the overflow.

---

[1]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

RESULTS OF TESTING PROGRAM

A loaded barge from the hydraulic dredge demonstration site on the Buffalo River was delivered to the disposal site on August 6, 1992, with the flocculation studies beginning the following morning (Figure 2). In order to simulate an "on barge" system of treatment, the suction pump head at the unloading dock was lowered into the barge to "sweep" the settled sediments from the barge bottom. This was done to resuspend the settled material to represent the percent solids normally associated with the water in the barge during loading.
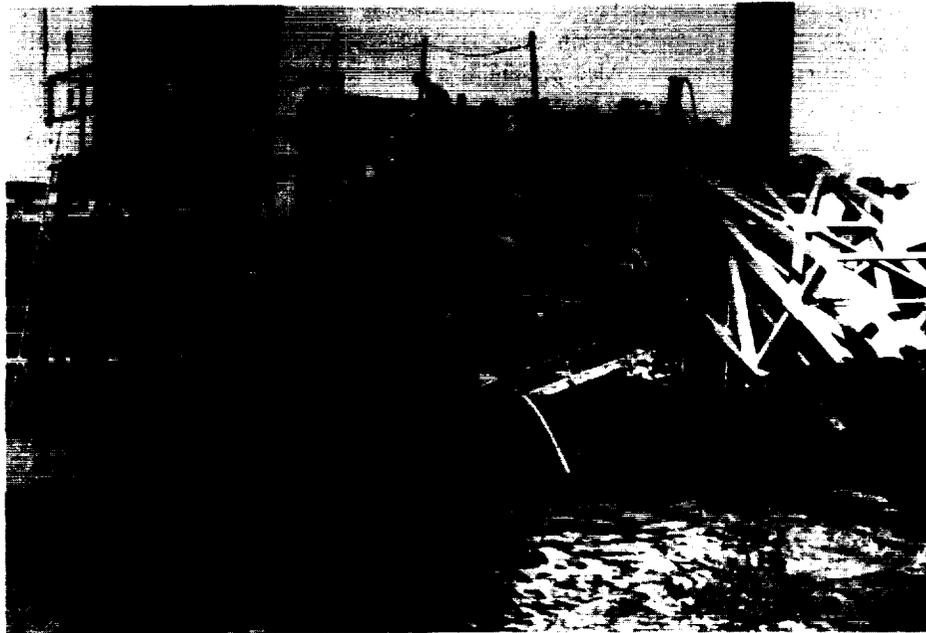

Figure 2. Suction feed line (4-in flexible) adjacent to the suction pump head of the loaded barge.

A series of three polymer concentrations was prepared during the study (0.02 pct, 0.03 pct, and 0.01 pct). This was accomplished by the addition of 5.04, 7.56, and 2.52 gal of 3.2 pct polymer to the polymer concentration tank. The tank was then filled to the 807-gal level with lake water to yield the desired polymer concentrations. The flow rates of the feed material from the barge and the flow rates of the discharge from the polymer concentration tank were determined by timing the movement of the fluids in the tanks and calculating the volume used. Figure 3 shows the polymer concentrate tank and pump.

Tables 1 through 3 indicate the polymer flow rate, feed rate, and percent solids of the feed for each series of tests. Cost of treating 1,000 gal of feed is based upon a polymer cost of $0.50/lb. For each series, the polymer concentration was held constant and the dosage was changed at 10 min intervals by varying the flow rate of the polymer. Samples of the overflow were also collected for determination of the NTU values. Over 200 gpm of feed being pumped into the clarifying tank created turbulent conditions which allowed some of the flocculated material to overflow with the clean water (Figure 4). For this reason, the overflow samples were allowed to settle for 8 min prior to making the NTU measurements.
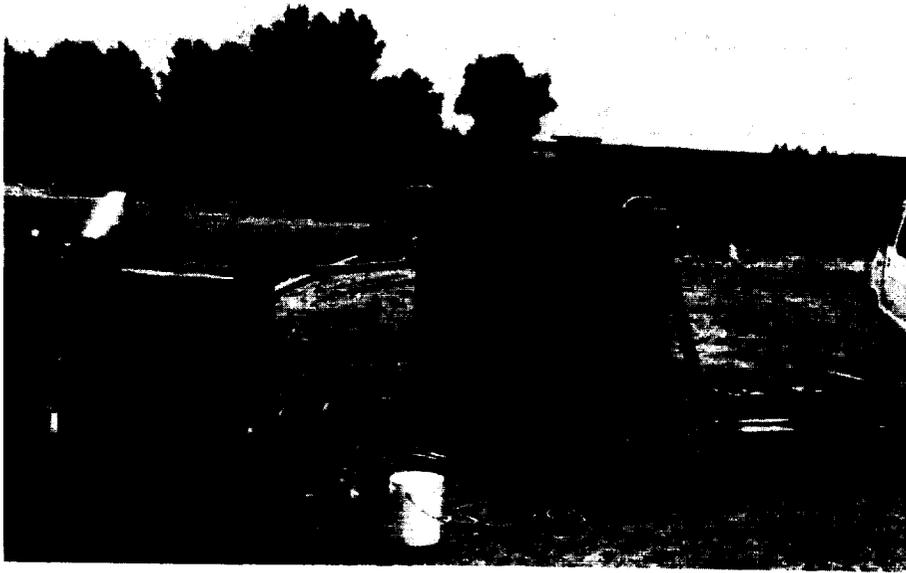
276

Figure 3. Small polymer pump on right beside concentrate
tank, large diesel powered pump on left, and 2,000 gal
clarifying tank in foreground with CDF beyond.

Table 1.--Test results for series 1 using the following conditions:
polymer concentration of 0.02 pct, feed rate of 241 gpm at 1.6 pct solids

Test number	Polymer dosage, gpm	Overflow, NTU	Cents per 1,000 gal of feed
1	19.87	17	8.23
2	16.90	15	7.01
3	11.51	13	4.78
4	7.06	17	2.93
5	3.96	13	1.64

Table 2.--Test results for series 2 using the following conditions:
polymer concentration of 0.03 pct, feed rate of 228 gpm at 1.5 pct solids

Test number	Polymer dosage, gpm	Overflow, NTU	Cents per 1,000 gal of feed
1	20.15	14	13.24
2	17.38	14	11.42
3	12.22	12	8.03
4	4.16	13	2.73
5	2.37	16	1.56

Table 3.--Test results for series 3 using the following conditions:
polymer concentration of 0.01 pct, feed rate of 219 gpm at 1.3 pct solids

Test number	Polymer dosage, gpm	Overflow, NTU	Cents per 1,000 gal of feed
1	20.43	12	4.66
2	17.91	12	4.08
3	12.11	13	2.76
4	6.96	15	1.59
5	2.27	27	0.52

Figure 4. Clarifying tank (2,000 gal) with 8-in to 6-in
overflow (top left) and 4-in underflow line (bottom right).

The NTU values remained relatively constant for all 3 series of polymer concentrations except for Series 3, Test 5, where a significant increase in the NTU values occur. It is at this point where insufficient polymer is added to feed material to flocculate all of the suspended solids.

A sample of the flocculated material from the underflow was collected to determine the percent solids. The underflow solids were approximately 31 pct by weight for test 5 of the series shown in Table 3. Figure 5 shows the clean water overflow from the clarifier along with the flocculated material being drained off with the underflow.

BIOASSAYS

One of the major concerns for utilizing a polymer treatment system and discharging the "clean" water back into the Buffalo River, is the effect the polymer would have on organisms living in the river. From the data shown in Table 3, Test 5, approximately 2.27 gpm of 0.01 pct polymer was added to the 219 gpm feed material entering the tank clarifier. This is equivalent to approximately 1 ppm of polymer being added to the feed material from the barge.

Bioassays were conducted by the Corps, Waterways Experiment Station, Environmental Laboratory, Vicksburg, MS. A sample of the feed (untreated water), along with 2 samples of the clean water overflow (polymer treated) from the tank clarifier were collected for the purpose of conducting biological studies to determine if the polymer had any toxic response on living organisms (Daphnia magna). The Daphnia magna were tested in glass beakers containing 250 mL of each sample and survival rates were determined over time. The data from the different tests are shown in Tables 4 through 6.

Table 4.--Survival of Daphnia magna (48 h exposure)

Treatment sample	Percent survival			
	Test 1	Test 2	Test 3	Test 4
Feed	90	80	90	70
Overflow - 1	100	100	90	100
Overflow - 2	90	80	90	100

Table 5.--Survival of Daphnia magna (96 h exposure)

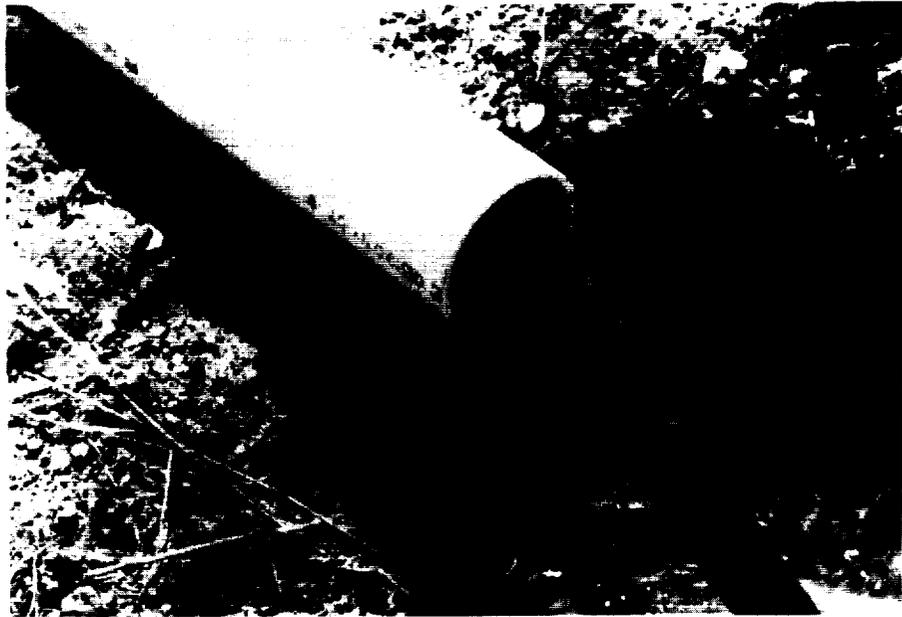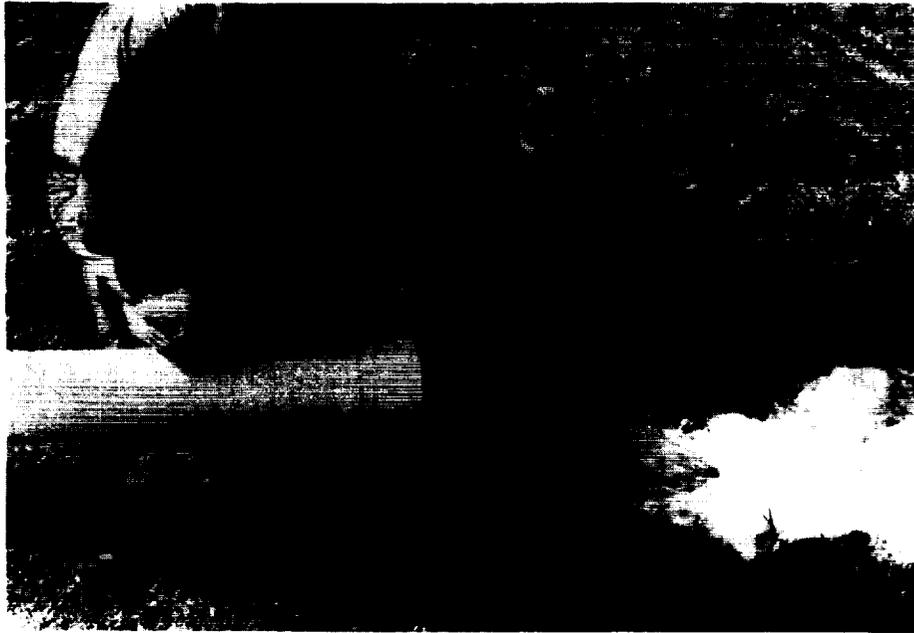| Treatment sample	Percent survival			
	Test 1	Test 2	Test 3	Test 4
Feed	20	10	10	0
Overflow - 1	60	50	40	50
Overflow - 2	50	60	50	40

Figure 5. "Clean" water overflow (top) beside flocculated
underflow material (bottom).

Table 6.--Duplicate test of survival of Daphnia magna (96 h exposure)

Treatment sample	Percent survival			
	Test 1	Test 2	Test 3	Test 4
Feed	50	90	100	80
Overflow - 1	50	80	70	80
Overflow - 2	20	60	70	30

From Table 4, at the end of 48 h, the Daphnia magna survival rate was higher in the treated water than the feed material. Table 5 data (96 h survival rate) shows similar results, with the survival rate in the feed diminishing to between 0 and 20 pct. Because of the higher indicated toxicity of the feed than the treated feed, another 96 h survival rate test was conducted with the results shown in Table 6. This second test seems to indicate higher survival rates in the feed and diminishing survival rates in the overflow samples.

The Daphnia did not thrive in any of these samples. However, because there are no clear cases where the data shows greater toxicity of the treated water than that of the feed, these test are inconclusive.

CONCLUDING REMARKS

Costs associated with the polymer requirements were calculated using $0.50/lb as the cost of the polymer. The NTU values remained relatively constant for all series of tests except the last test of Series III (Test No 5) with the NTU values increasing to 27. This most likely represents the transition point for complete flocculation of the particulate matter, with this NTU value still likely to be lower than the required regulatory level. This represents a cost of approximately $0.0052 per 1,000 gal of feed or $5.20 for 1,000,000 gal. Figure 6 shows a conceptual drawing of how this technique could be used as the dredge is operating.
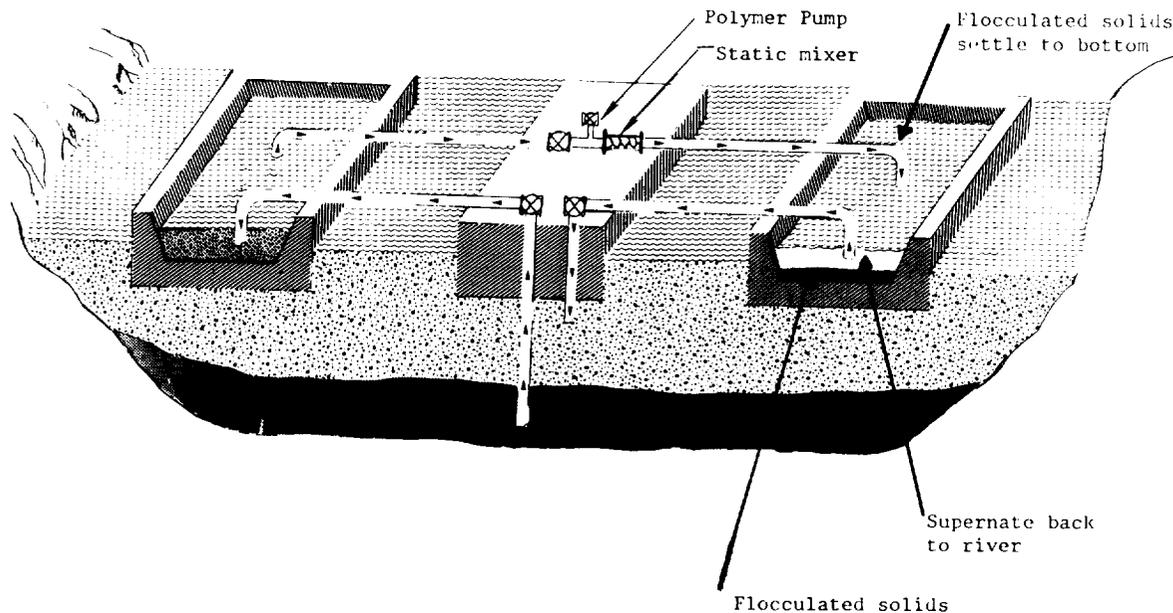

Figure 6. Flowsheet for continuous operation of flocculation system.
(1) River sludge to holding barge; (2) suspended solids treated with polymer to holding barge; and (3) flocculated solids settle to bottom and supernate pumped into the river.

281

REFERENCES

1. Environmental Protection Agency, Assessment and Remediation of Contami- nated Sediments (ARCS) Program - An Overview, Environmental Fact Sheet, United States Environmental Protection Agency, Great Lakes National Program Office, 77 West Jackson Blvd. Chicago, IL 60604, July 1992.

2. Sharma, Sandeep K., and B. J. Scheiner, Effect of Physico-Chemical Parameters on Dewatering: A Case Study, Fluid/Particle Separation Journal, v. 4, No. 3, September 1991, pp. 162-165.

MATERIALS
SCIENCE

BENCH-SCALE SYNTHESIS OF NANOSCALE MATERIALS

M. F. Buehler
Pacific Northwest Laboratory
Richland, Washington 99352

J. G. Darab
Pacific Northwest Laboratory
Richland, Washington 99352

D. W. Matson
Pacific Northwest Laboratory
Richland, Washington 99352

J. C. Linehan
Pacific Northwest Laboratory
Richland, Washington 99352

ABSTRACT

A novel flow-through hydrothermal method used to synthesize nanoscale powders is introduced by Pacific Northwest Laboratory. The process, Rapid Thermal Decomposition of precursors in Solution (RTDS), uniquely combines high-pressure and high-temperature conditions to rapidly form nanoscale particles. The RTDS process was initially demonstrated on a laboratory scale and was subsequently scaled up to accommodate production rates attractive to industry. The process is able to produce a wide variety of metal oxides and oxyhydroxides. The powders are characterized by scanning and transmission electron microscopic methods, surface-area measurements, and X-ray diffraction. Typical crystallite sizes are less than 20 nanometers, with BET surface areas ranging from 100 to 400 m^2/g. A description of the RTDS process is presented along with powder characterization results. In addition, data on the sintering of nanoscale ZrO_2 produced by RTDS are included.

INTRODUCTION

Industrial demand for advanced materials has motivated the development of new methods to produce ultrafine powders. Ultrafine powders, also known as nanocrystalline or nanoscale powders, are defined here as those having crystallite sizes of the order of 1 to 100 nanometers. These powders can be used as feedstocks to fabricate materials such as cost-effective catalysts, high-performance components for aerospace and power generation applications, and lightweight/high-strength automotive materials. Ultrafine powders offer distinct advantages over more common microcrystalline powders because they provide high grain boundary area and/or high specific surface area. Unfortunately, common synthesis methods to produce nanoscale powders do not provide production rates sufficient to accommodate industrial needs. In this paper, we describe a hydrothermal process developed at Pacific Northwest Laboratory (PNL) that economically produces nanocrystalline oxide and oxyhydroxide powders at high rates suitable for industrial applications. The process is called Rapid Thermal Decomposition of precursors in Solution (RTDS).

Powders produced by the RTDS process are making an impact in many industries, an important example is in the field of heterogeneous catalysis. Often, the cost of bulk catalyst material may be high, but for ultrafine material having a high specific surface area, the cost per active surface site is very low. This reduces both capital and operating costs. As will be shown in this paper, the

PAGE 284

flexibility of the RTDS process allows the powder to be used as catalyst material and as precursors for the fabrication of advanced materials. In the latter application, RTDS powders offer the ability to control the microstructure of a consolidated advanced material which enhances certain mechanical properties.

POWDER SYNTHESIS

Several existing synthesis methods can produce nanoscale powders. Some of the more common nanocrystalline powder synthesis methods are gas-phase condensation, sol-gel processing, and combustion synthesis (1). However, all of these processes have limitations for industrial applications, in particular, low production rate of the powder product. These methods are briefly summarized below.

Gas-phase condensation was first suggested by Gleiter (2) and uses an ultrahigh vacuum system fitted with a heating assembly and a liquid-nitrogen-filled cold finger. Unfortunately, the gas phase condensation process is inherently a batch operation and the production rates are low for industrial standards. Although this process is not yet generally useful in industrial applications, it has enabled researchers to demonstrate the improved room-temperature mechanical properties of nanoscale materials relative to their coarse-grained counterparts (3-5).

Sol-gel technology is a chemical method used to produce oxide material, including ultrafine powders, at room temperature. However, relatively pure precursors for industrially important materials such as nickel, iron, chromium, and zinc oxide are either very expensive or must be synthesized in-house prior to sol-gel processing. In addition, many of the precursors are moisture sensitive, making them difficult to store and handle.

Combustion synthesis combines soluble metal salts and a complexant/fuel such as carboxylate azides, urea, or glycine (6-10). The mixture is heated, and an autoignition reaction occurs which produces the desired powder. This technique is useful for the production of ceramic powders with specific stoichiometry and also for multicomponent systems. However, the technique does not easily yield hydroxides, and the distribution of grain-sizes is large. Also, the powders produced by this method are highly aggregated into hard clusters or agglomerates.

RTDS is a new, flow-through hydrothermal process with the capability to continuously produce nanocrystalline powders at rates of pounds per day using a bench-scale apparatus (11). The RTDS process was recently recognized for its innovative contribution to powder synthesis by receiving the prestigious R&D 100 award for 1993 (12). The process offers a flexibility to control the crystallite size and uniformity while producing powders at high rates.

RAPID THERMAL DECOMPOSITION OF PRECURSORS IN SOLUTION

Process Description

The synthesis of RTDS nanoscale powders begins with a feedstock solution of a metal salt or mixture of metal salts dissolved in water. The bench-scale system primarily consists of a high-pressure pump, a heated region, and a pressure reduction nozzle. The liquid feedstock is pressurized by a reciprocating piston pump and heated to reaction temperature by a standard-tube furnace. Within the heated region, hydrothermal (forced hydrolysis) reactions occur that produce solid oxide and oxyhydroxide particulates. Typical RTDS operating conditions include pressures ranging from 5000 to 8000 psi and temperatures from 200°C to 400°C. After the particles are formed in the heated region, the resulting suspension passes through a pressure reduction orifice. The solid/liquid aqueous suspension is then either used in slurry-based processes or the particulates are separated and dried by standard industrial methods (sedimentation, centrifugation, spray drying, etc.). The RTDS process is shown schematically in Figure 1. Although the present

286

RTDS system is a bench-scale apparatus, the technology uses standard unit operations which can readily be incorporated into existing industrial facilities.

A key feature of the RTDS process is that the nuclei are formed quickly and are allowed very little time to grow in the hydrothermal region. Typical residence time of the solutions in the heated region ranges from 2 to 30 seconds. This variable can be controlled by either changing the length of tubing within the heated region or varying the flow rate. As a result of the short residence time, crystallite sizes produced by this method are limited to the nanometer range. The particles produced are typically aggregates of nanometer-sized crystallites and are of the order of 100 nanometers. Some control over crystallite size can be exercised by adjusting the residence time of solution in the heated zone.
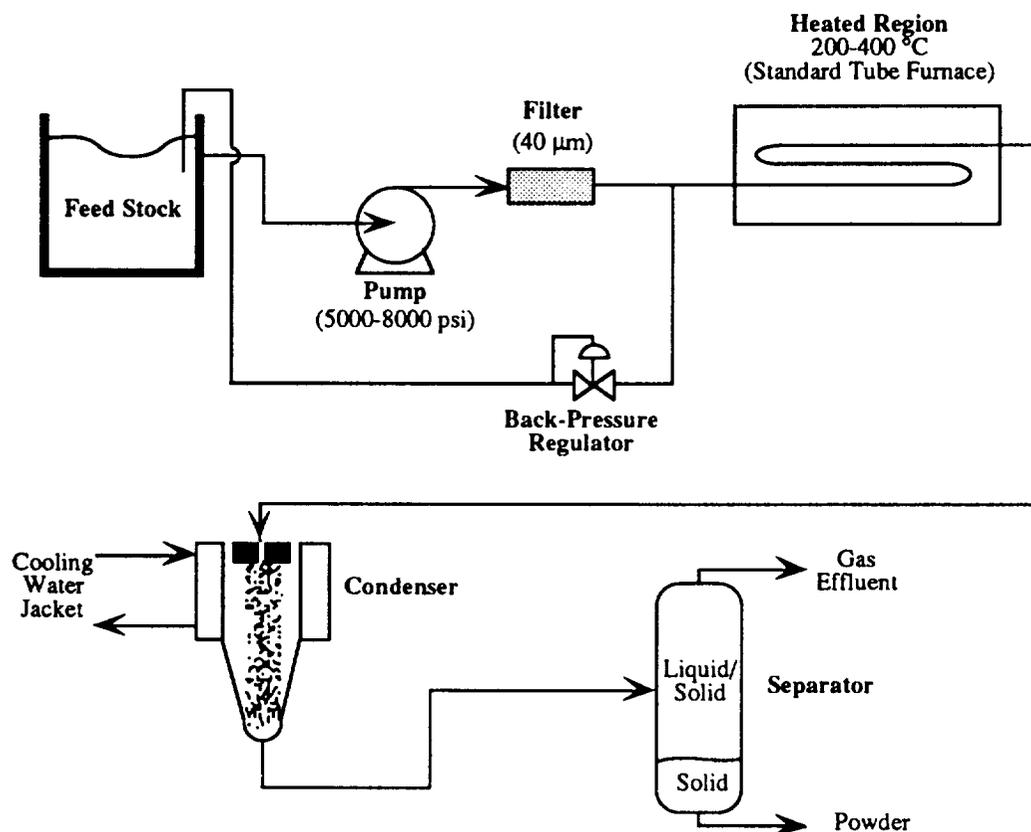

Figure 1. Schematic diagram of the RTDS process.

Powder Characterization

The RTDS powders have been characterized by several techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Brunauer-Emmett-Teller (BET) nitrogen adsorption analysis. The XRD measurements, which allow phase identification and provide crystallite size information, were obtained using a Philips 3000 series X-ray diffractometer with a copper source operated at 40 kV and 45 mA. SEM was performed on an ElectroScan MEM-20 multi-environmental electron microscope. Both bright-field and dark-field TEM micrographs were obtained using a Philips EM400T electron microscope with a 120 keV electron beam. The BET surface area measurements were performed on a Micromeritics ASAP 2000 using multipoint analysis. Some of the powders produced using the RTDS method

and the corresponding crystallite sizes (determined by XRD line broadening analysis) are shown in Table 1.

Table 1. Typical powders produced by the RTDS process.

Material	Chemical Formula	Crystallite size (nm)
Ferrihydrite	$5Fe_2O_3 \cdot 9H_2O$	<10
Hematite	$\alpha\text{-}Fe_2O_3$	23
Magnetite	Fe_3O_4	12
Tenorite	CuO	20
Trevorite	$NiFe_2O_3$	<10
Bunsenite	NiO	12
Zirconia	ZrO_2	<10
Zincite	ZnO	34
Anatase	TiO_2	<10

Figure 2 shows a composite bright-field TEM micrograph of iron oxyhydroxide/oxide powders produced at three different RTDS processing temperatures from an iron nitrate solution. This figure clearly illustrates that RTDS operating conditions affect the characteristics of the resulting powders. In this example, both crystallite size and phase were affected by changes in the RTDS processing temperature. These observations are confirmed by analysis of the XRD patterns for these three materials (Figure 3). The XRD patterns show peak width broadening with decreasing temperature, which indicates a reduction in crystallite size. The XRD measurements were also used to identify the phases present. The predominant phase at the lower RTDS processing temperature (200°C) was 6-line ferrihydrite, while at high temperatures (greater than 350°C) the predominant phase was hematite. A mixture of these two phases was produced at intermediate temperatures.

The BET surface-area measurements of RTDS powders typically range from 100 to 400 m²/g. For example, the 6-line ferrihydrite shown in Figure 2 has a specific surface area of 280 m²/g. Other high surface area RTDS powders of industrial importance include: zirconia = 428 m²/g, anatase = 136 m²/g, and hematite = 153 m²/g.

Suspensions of nanocrystalline materials produced by RTDS provide unique feedstocks for spray drying. Using this method, micrometer-scale spherical aggregates of nanocrystallites are readily produced. Figure 4 shows a SEM micrograph of a ZrO_2 powder produced by spray drying a RTDS-generated suspension of ZrO_2. The drying process yielded solid-core spherical aggregates in the 0.5-μm to 5-μm size range. The morphology of the spray-dried powder is ideally suited for subsequent consolidation processes, such as powder injection molding, isostatic compaction, or hot pressing.

POTENTIAL COMMERCIAL APPLICATIONS FOR RTDS POWDERS

Catalysts

The RTDS powders are an attractive option for heterogeneous catalysts because of their high degree of crystallinity and high specific surface areas. RTDS powders typically do not need to undergo pretreatment steps (such as increasing the number of acidic sites) before becoming

288

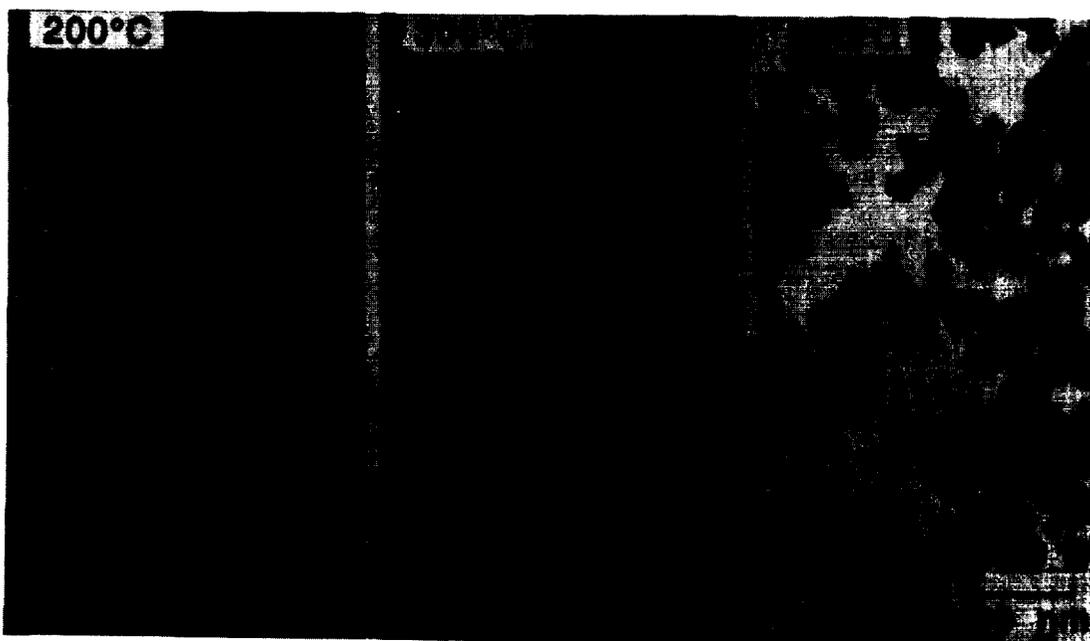**RTDS Powders Produced from 0.1M Fe(NO₃)₃ Solutions**

Figure 2. TEM micrographs of RTDS powders produced from iron nitrate solutions at 200°C, 300°C, and 350°C.
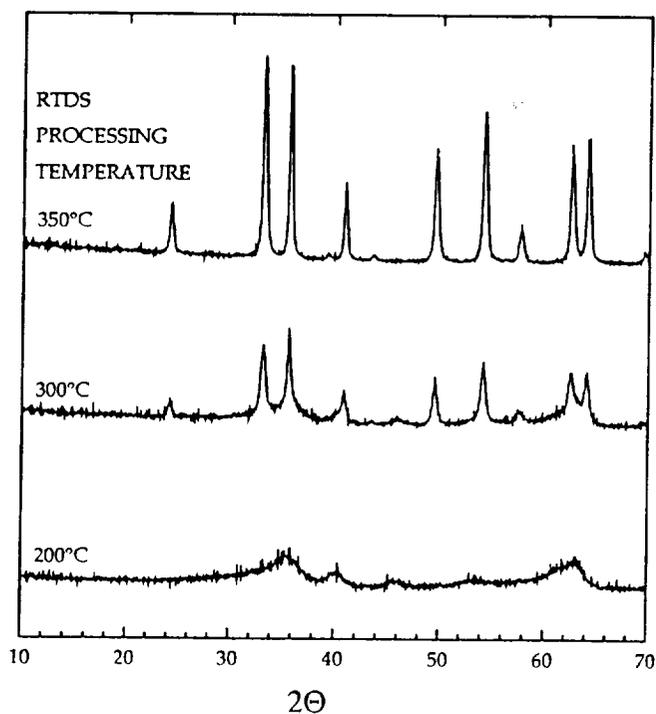

Figure 3. The corresponding XRD patterns for the RTDS powders shown in Figure 2.

"activated" catalysts. For many applications, the RTDS production conditions can be tailored to simultaneously synthesize and pretreat the catalyst powder so that the powder is "preactivated" when collected. RTDS powders can also be consolidated and sintered into porous, high surface area supports for catalysts, or catalyst and support material precursors can be co-processed in the RTDS apparatus to yield a pre-formed supported catalyst.

RTDS powders and supports were tested by workers at PNL and by their industrial clients. Nanoscale RTDS ferrihydrite powder, similar to that shown in Figure 2, was used as a coal liquefaction catalyst, and the activity of the RTDS produced powders was compared with other commercially available catalysts. The RTDS material yielded more liquefied products than any of the other iron-based catalyst tested.
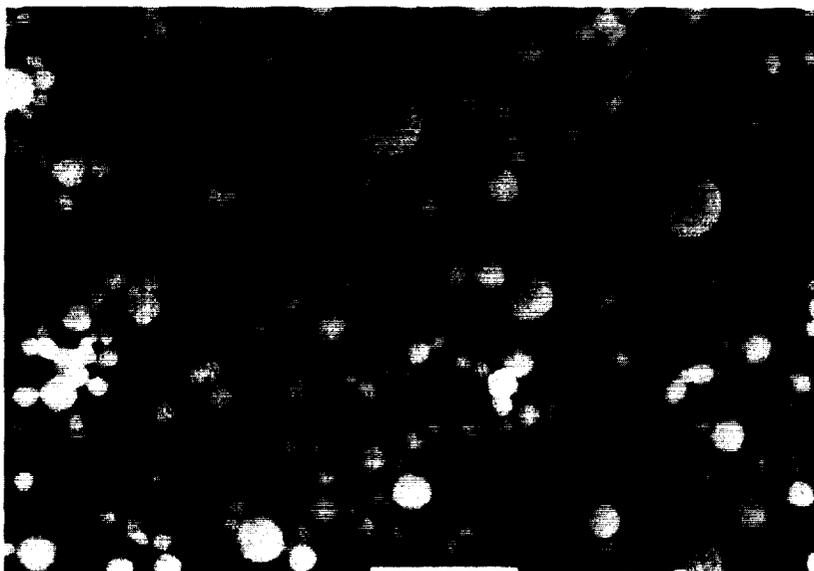

Figure 4. SEM of a spray-dried ZrO_2 powder produced using a ZrO_2 suspension generated by RTDS processing of a zirconyl nitrate solution at 300°C.

Powder Manufacturing of Components

The properties of nanoscale powders are dominated by their small crystallite size and high interfacial area (i.e., high grain boundary area and/or high surface per unit mass). Therefore, the interfacial mechanism of mass transport under certain processing conditions will control the microstructure of a component produced from a powder precursor. The ability to control the microstructure of the bulk product is advantageous because the physical properties of the material are dependent on the grain size and microstructure of the bulk material. Consequently, nanocrystalline powders provide a unique opportunity to control the microstructure of a fabricated component.

Interfacial phenomena are important when powders are fabricated into bulk materials by consolidation and sintering (13). In conventional powder processing, powders are consolidated into a desired component geometry under high pressure. Subsequently, the component is heated at high temperature (sintered) to produce a part with little porosity. The sintering kinetics for a nanocrystalline powder compact are dominated by grain boundary diffusion because of the extremely high grain boundary areas. In contrast, for microcrystalline powder compacts, volume diffusion typically dominates the sintering kinetics. The activation energy for grain boundary diffusion is lower than that of volume diffusion for nanoscale compacts. Therefore, the lower

activation energy provides nanocrystalline powder compacts with lower sintering temperatures as compared with conventional microcrystalline powder compacts. This fundamental difference in the sintering mechanism also provides an alternative pathway to control the microstructure of the bulk monolith.

The importance of microstructural control in materials is demonstrated by examining the relationship between the mechanical properties of a material and its microstructure. The yield strength and the fracture strength of a polycrystalline material are related to grain diameters in the bulk material by similar expressions:

$$\text{Strength} = K_1 + \frac{K_2}{d^{1/2}} \qquad [1]$$

where K_1 is a materials-related constant, K_2 is a collection of appropriate constants, and d is the grain diameter (14). Clearly, smaller grain size improves the strength of such materials.

Creep deformation, or time-dependent strain under an applied stress, is also related to grain size in the bulk material by the relation:

$$\text{Creep Rate} \propto \frac{1}{T\,d^3} \qquad [2]$$

where T is the temperature (15). From Equation 2, the smaller the grain diameter of the material, the lower temperature is required to provide a given creep rate. This is important for nanocystalline material because creep deformation occurs at lower temperatures, and, therefore, grain boundary rearrangement occurs without grain growth. Also, superplastic forming of nanocrystalline bulk materials becomes more feasible as grain size is decreased (15).

RTDS nanoscale powders can be consolidated and sintered into useful components, often with unique properties. Researchers at PNL and their clients are currently investigating the agglomeration, consolidation, and sintering behaviors of a variety of single and multi-phase RTDS powders. Figure 5 is a plot of relative sintered density as a function of normalized temperature showing two regions: one for nanocrystalline zirconia and the other for microcrystalline zirconia (16). Region I defines an area where 10 nanometer crystallite microstructure will sinter under typical conditions. Region II describes a similar area for 200 nanometer crystallites, which is typical of many conventional microcrystalline oxide systems. Figure 5 also shows sintering characteristics of zirconia produced by the RTDS process.

The RTDS zirconia sintering data fall well within Region I and densifies at lower normalized temperature than the microcrystalline counterpart. The reduction in sintering temperature for the RTDS powder is due to the difference in mass-transport mechanisms and activation barriers associated with each microstructure grain size. Darab *et al.* (13) have shown that the mechanism of sintering for nanocrystalline RTDS zirconia is grain boundary diffusion with an activation barrier of 250 kJ/mol, whereas that of microcrystalline powders is volume diffusion with an activation barrier of 430 kJ/mol. The lower sintering temperatures associated with nanoscale powders can provide significant energy savings when used as a feedstock for powder manufacturing processes.

SUMMARY

The RTDS process enables the production of nanoscale, crystalline oxide/oxyhydroxide powders at industrial-scale rates. The flexibility of the process allows control over the crystalline size and phase. Other synthesis methods are limited by low production rates, and RTDS fills an existing gap in industrial powder production. The powders produced by RTDS have been shown to be

effective catalysts for coal liquefaction and provide lower sintering temperature for zirconia compacts. The bench-scale apparatus is easily scaled to pilot-scale level because the process uses standard industrial unit operations. It is anticipated that the RTDS process will produce unique advanced materials for numerous applications, such as: 1) powders for pigments, magnetic media, and abrasives; 2) additives for advanced composites; and 3) starting materials for the preparation of separation media such as nanoporous filters.
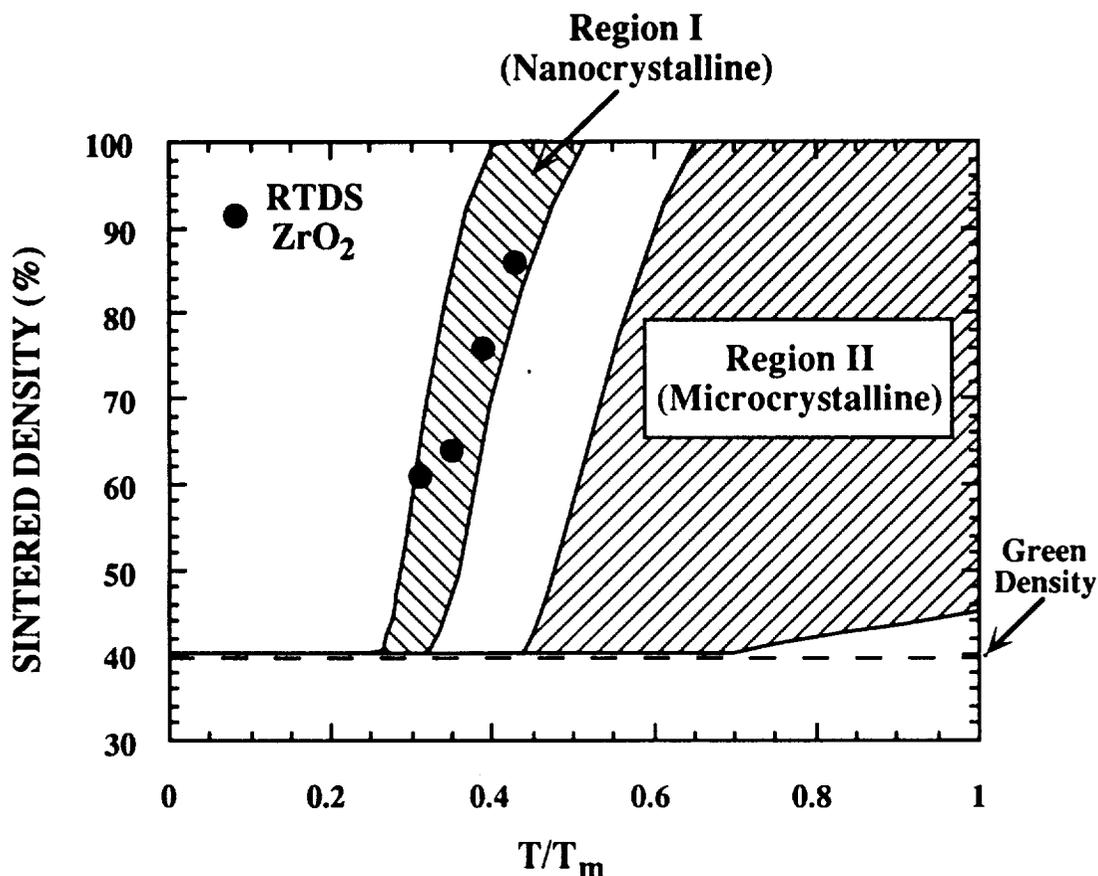

Figure 5. Relative sintered density as a function of normalized temperature (T_m = 2570°C) for nanocrystalline RTDS ZrO_2 and theoretical behavior.

ACKNOWLEDGMENTS

REFERENCES

1.) Williams, J. C., and Kear, B. H., "Research Opportunities for Materials with Ultrafine Microstructures," National Materials Advisory Board, National Academy Press, NMAB-454, 1989.

2.) Gleiter, H., "Deformation of Polycrystals: Mechanisms and Microstructures," Eds. N. Hansen *et al.*, Riso National Laboratory, Roskilde, p.15, 1981.

3.) Averback, R. S., Hofler, H. J., Hahn, H., and Logas, J. C., *NanoStructured Mat.*, **1**, 173 (1992).

4.) Nieman, G. W., Weertman, J. R., and Siegel, R. W., *J. Mat. Res.*, **6**, 1012 (1991).

5.) Siegel, R. W., Ramasamy, S., Hahn, H., Zongquan, L., Ting, L., and Gronsky, R., *J. Mat. Res.*, **3**, 1367 (1988).

6.) Ravindranathan, P., and Patil, K. C., *J. Mat. Sci. Letters*, **5**, 221 (1986).

7.) Ravindranathan, P., and Patil, K. C., *Am. Cer. Soc. Bull.*, **66**, 668 (1987).

8.) Ravindranathan, P., Mahesh, G. V., and Patil, K. C., *J. Solid State Chem.*, **66**, 20 (1987).

9.) Kingsley, J. J., and Patil, K. C., *Materials Letters*, **6**, 427 (1988).

10.) Chick, L. A., Pederson, L. R., Maupin, G. D., Bates, J. L., Thomas, L. E., and Exarhos, G. J., *Materials Letters*, **10**, 6 (1990).

11.) Matson, D.W., Linehan, J. C., and Bean, R. M., *Materials Letters*, **14**, 222 (1992).

12.) Buehler, M. F., Matson, D. W., Linehan, L. C., Phelps, M. R., Neuenschwander, G. G., Fulton, J. L., and Bean, R. M., *R & D Magazine*, **35**, 57 (1993).

13.) Darab, J. G., Buehler, M. F., Linehan, J. C., and Matson, D. W., submitted to *Part. Sci. and Tech*, 1993.

14.) Dieter, G. E., Mechanical Metallurgy, 3rd Ed., McGraw-Hill, New York, Chapters 6 and 7, 1986.

15.) Kingery, W. D., Bowen, H. K., and Uhlmann, D. R., Introduction to Ceramics, John Wiley and Sons, New York, p. 704, 1976.

16.) Ashby, M. F., HIP-Maps, Version 6.0, Personal Computer Program, University of Cambridge CB2 1PZ, England, 1990.