ORNL-2509
Reactors - General

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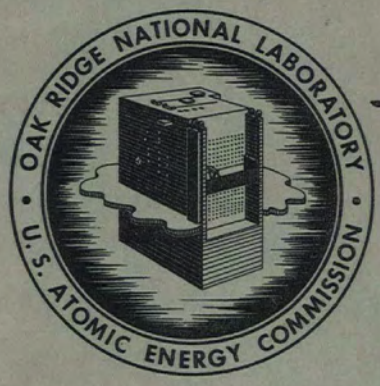

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Washington 25, D. C.

ORNL-2509
Reactors - General

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section A

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R. L. Pearson, K. H. McCorkle, C. V. Ellison, P. A. Haas

DATE ISSUED

MAY 26 1958

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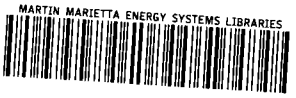

ABSTRACT

The flowsheet for making thorium oxide in 284-lb batches provides for adding 1 M oxalic acid to 1 M $Th(NO_3)_4$ cooled to 10°C. The oxalate is digested, washed, and step-calcined to 1600°C for 4 hr. After classification the final product has an average particle size close to 1 μ with less than 2 wt % larger than 5 μ. In laboratory studies thorium oxalate prepared by adding oxalic acid solution to thorium nitrate solution was more uniform and had a smaller average particle size than that prepared by mixing the solutions in reverse. The average particle size of the oxide decreased with decreasing oxalate precipitation temperature and increasing reagent concentration. More uniform oxides were produced by lower oxalate precipitation temperatures, and the fraction of oversize particles decreased with increasing stirring rate and reagent addition rate. Nearly all the particles that sintered due to packing when fired to 1600°C for 4 hr were released by steeping and agitation in oxalic acid at pH 2.6.

CONTENTS

1.0 INTRODUCTION

The preparation of thorium oxide was investigated to determine conditions that produce ThO_2 suitable for use in the homogeneous reactor blanket. The particle shape, size distribution, and temperature at which thorium oxide is fired influence the rheological and erosive properties of aqueous thoria slurries. In the thorium concentration range 660-1350 g/kg D_2O, optimum for a two-region thorium breeder reactor blanket, particles above 5 μ erode the container surface too rapidly for use, and slurries whose average particle size is less than 1.5 μ have excessive yield strengths.

Large quantities of sized oxide to meet varying specifications were needed for tests designed to determine the specifications for the slurry to be used in the blanket of HRE-3. Both the present flowsheet and laboratory tests on which it was based are discussed.

The authors acknowledge the assistance received from the Analytical Chemistry Division, particularly G. W. Leddicotte and W. R. Laing, and from C. E. Schilling, D. E. Ferguson, J. P. McBride in the Chemical Development Section and W. T. McCarley and E. M. Shank in the Pilot Plant Section of the Chemical Technology Division.

2.0 PROCESS DESCRIPTION

2.1 Chemical Process Flowsheet

In the present flowsheet (Fig. 1) for making thorium oxide in the Chemical Technology Division Pilot Plant, 1 M solutions of thorium nitrate and oxalic acid are mixed in an agitated tank with controlled temperature, addition rate, and order of addition. Typically, all the thorium nitrate is added to the precipitator, after which the oxalic acid solution is added over a period of 3 hr with the reagents held at 10°C by external cooling. The slurry of precipitated thorium oxalate is digested 6 hr at 85°C and then pumped to a vacuum filter where the solid is separated from the mother liquor and washed three times with demineralized water. The oxalate cake on the filter is air-dried and is then loaded on trays for the first calcination.

In the first calcination the air-dried thorium oxalate is heated successively at 180°C for 2 hr, at 380°C for 2 hr, and at 650°C for 1.75 hr. The material is then packed into a platinum tray for the second calcination and fired at 1600°C for 4 hr.

The 1600°C calcined thorium oxide contains a certain fraction, typically 10%, of particles larger than desired. These oversize particles are removed by classification, i.e., by suspension of the thorium oxide in oxalic acid solution to an initial ThO_2 concentration of 160-200 g/liter. Dispersion is

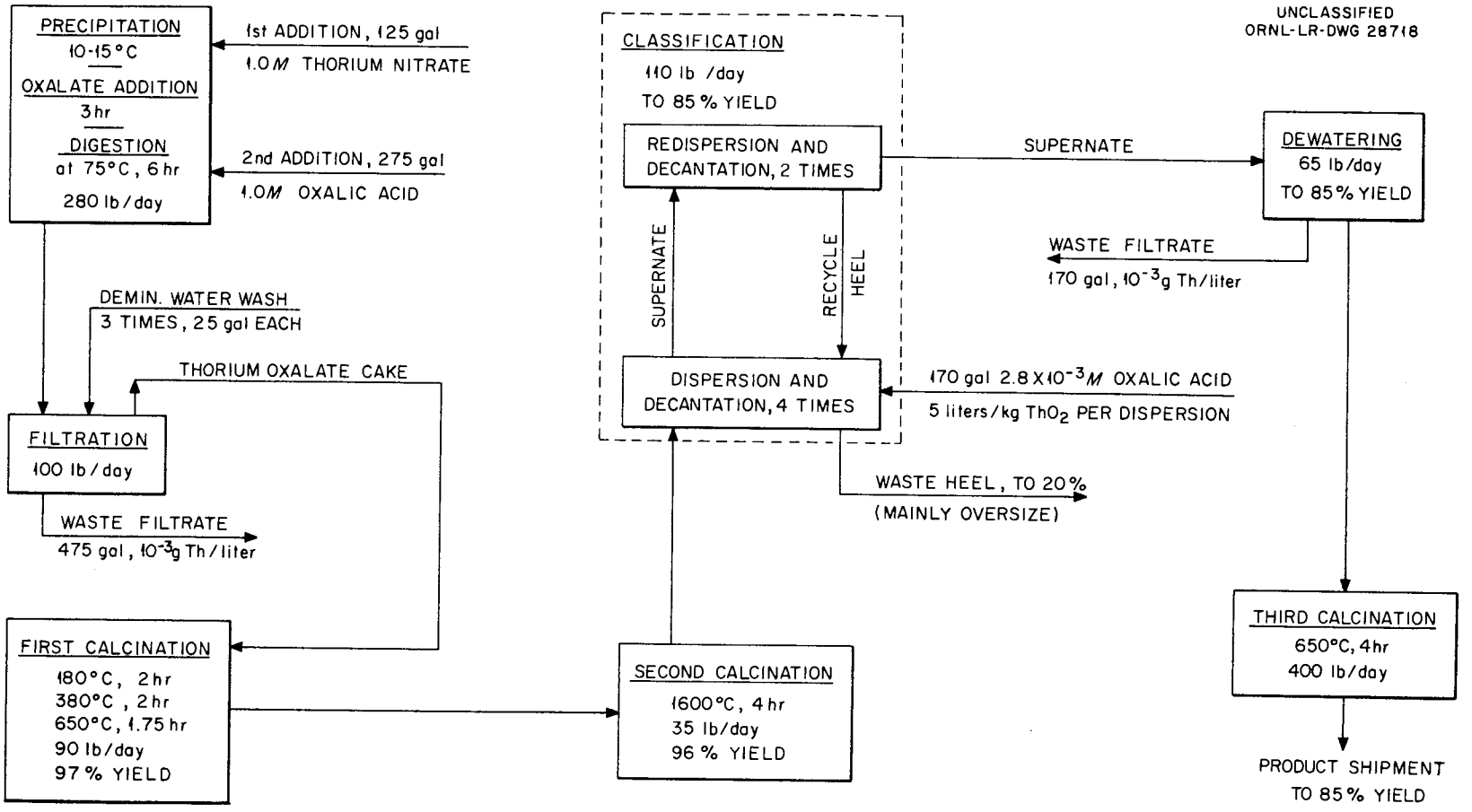

Fig. 1. Thorium Oxide Pilot Plant Chemical Flowsheet. Per cent yields based on initial thorium input, throughput based on pounds of thorium oxide per day.

maximum in a solution of pH 2.6. The suspension is stirred and the heel raked for 30 min, and the mixture is then allowed to stand for 1 min before the supernate is drawn off. Material coarser than 5-6 μ effective Stokes' settling diameter is rejected when the supernate withdrawal rate is set at 0.5 in./min liquid level drop. The withdrawn thorium oxide is dispersed and decanted again to ensure removal of oversized particles. The thorium oxide that settles to the bottom is also redispersed and decanted three more times to recover the considerable fraction of the fine particles that settle with the heel or are imperfectly dispersed. This procedure removes all but 1 or 2% of the thorium oxide smaller than the desired particle size.

The supernates are pumped to the centrifuge at a rate of 0.5 liter/min, and the centrifuge cake is recalcined at 650°C for 4 hr to destroy the oxalate adsorbed on the oxide.

The classification procedure is based on Stokes' law. In a suspending medium the rate of fall of a particle is proportional to its radius squared, $v = Cr^2$. This law holds only for a dilute suspension where the particle can fall freely. If the ThO_2 concentration is below 200 g/liter, Stokes' law holds sufficiently.

The classification step was added to the flowsheet after several loop runs at Y-12 with a slurry containing oversize particles, in which erosion was excessive. Within 40 hr after the slurry was added to the loop, the pump impellers and bearings had been so eroded that it was necessary to shut down the pump.

A particle size distribution of typical oxide before and after classification and a chemical analysis of sample LO-39 are shown in Fig. 2 and Table 1.

Table 1. Chemical Analysis of ThO_2 Product

Sample: LO-39

Contaminant	Amount	Contaminant	Amount
CO_3	0.06%	Cr	10 ppm
C_2O_4	<0.01%	Pb	<10 ppm
NO_3	<10 ppm	Na	<10 ppm
SO_4	<10 ppm	K	<10 ppm
PO_4	50 ppm	Li	<10 ppm
Si	<10 ppm	Ca	9 ppm
Cl	<10 ppm	Ba	< 2 ppm
Fe	54 ppm	Total rare earths	<50 ppm
Ni	19 ppm		
Loss on ignition	0.11%		
Surface area	1.8 m^2/g		
Crystallite size	>2500 A		

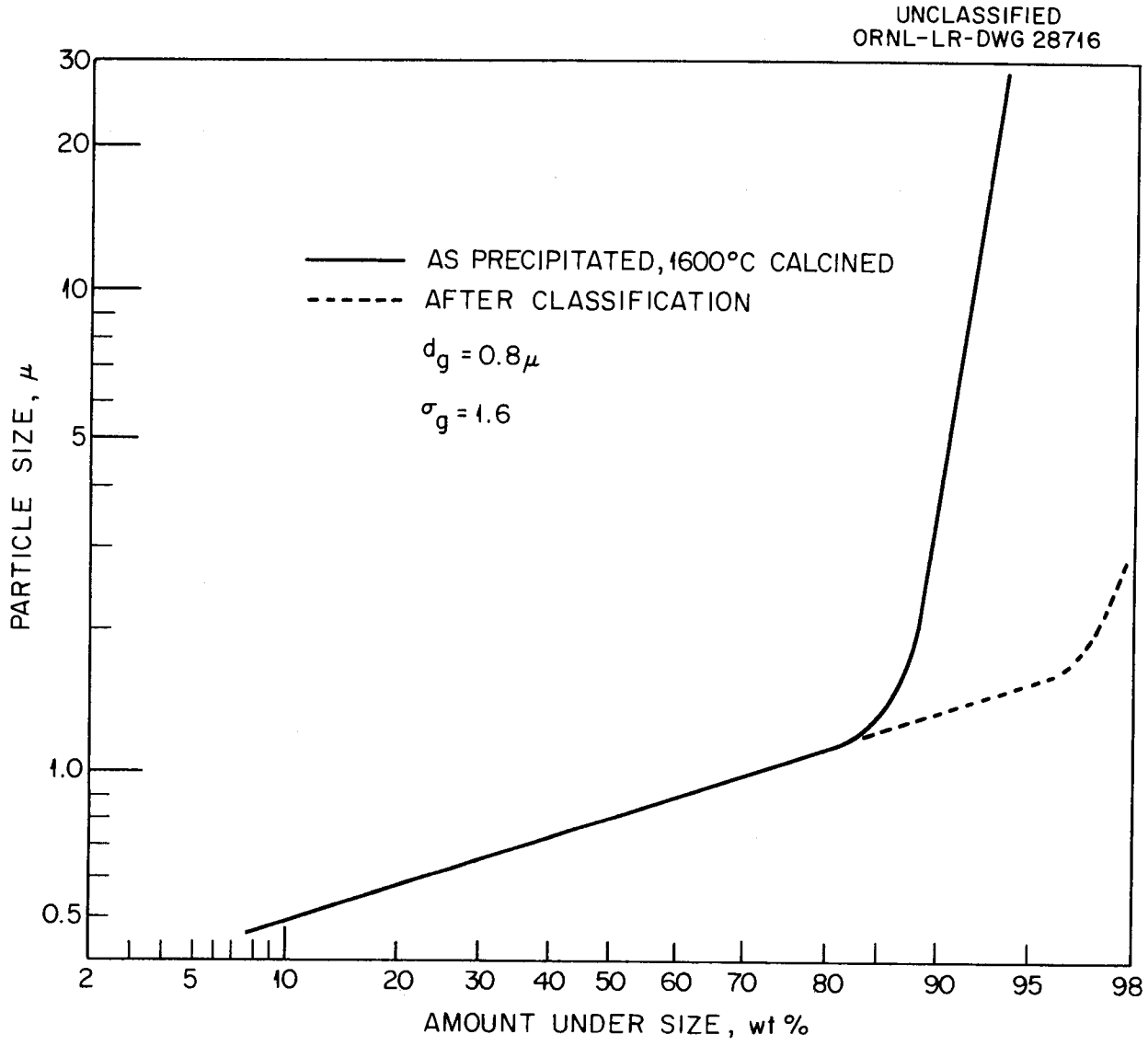

Fig. 2. Effect of Classification on ThO_2 Particle Size Distribution.

2.2 Equipment Flowsheet

The paths of the process streams through the major pieces of equipment are shown schematically in Fig. 3. Thorium nitrate is made up beforehand in the precipitation tank (B-20). Oxalic acid is made up in tank A-10, filtered, and pumped at a controlled rate into B-20. During the reaction the temperature is controlled by cooling coils containing Freon. After the reaction and digestion are completed, the resulting slurry is pumped to the filter (C-10) where the mother liquor is removed from the thorium oxalate, and the oxalate cake is washed with warm demineralized water from the water heater (C-11). Filtrate from C-10 is drawn into the receiver (C-20) by vacuum applied through a sight-glass chamber (C-21).

When the oxalate cake has been air-dried, it is removed with flat-bladed hand scoops and loaded into fused quartz trays which are placed in the electric furnace (D-10). The thorium oxide resulting from calcination of the oxalate in D-10 is reloaded into a platinum tray and is refired in the gas furnace (D-20).

The oxide is then weighed and dumped into the first decantation tank (E-10), where it is dispersed in dilute oxalic acid and decanted at a controlled rate. The supernatant from E-10 drains by gravity to the second decantation tank (E-11), where the slurry is redispersed and redecanted at a controlled rate to the product receiver tank (E-21). The contents of E-21 are pumped to the centrifuge (E-20), where the classified oxide is removed from the centrifuge batchwise by hand. Waste supernatant from E-20 passes through a sight glass to a waste holding tank (E-22), where it is sampled before final disposal.

Classified oxide is freed of residual oxalate by recalcining in the electric furnace (D-10).

Proposed Change in Calcination System. Fused silica trays are used for loading the oxalate in the electric furnace. These trays are subject to thermal shock, which silica does not resist well. Nickel trays appear to be a feasible alternative to silica trays although their use is not contemplated at present. In laboratory tests nickel formed an oxide coating which protected the metal from attack by both the atmosphere and the thorium oxalate. The oxide product fired in nickel contained 10 ppm of nickel.

A clay-bonded alumina crucible (Tycor, Chas. Taylor Sons Co.) with a 6-mil platinum liner will replace the platinum tray now used for loading oxalate in the 1600°C furnace. This will increase the total container capacity 2.4-fold. An unlined crucible was successfully fired to 1600°C on a 24-hr cycle, but it contaminated the oxide.

Proposed Change in Classification System. A new classification system (Fig. 4) is being constructed. The oxide heel in the first decantation tank (E-10) will be dispersed by a 0.75-hp turbine-blade Lightnin agitator (E-10A).

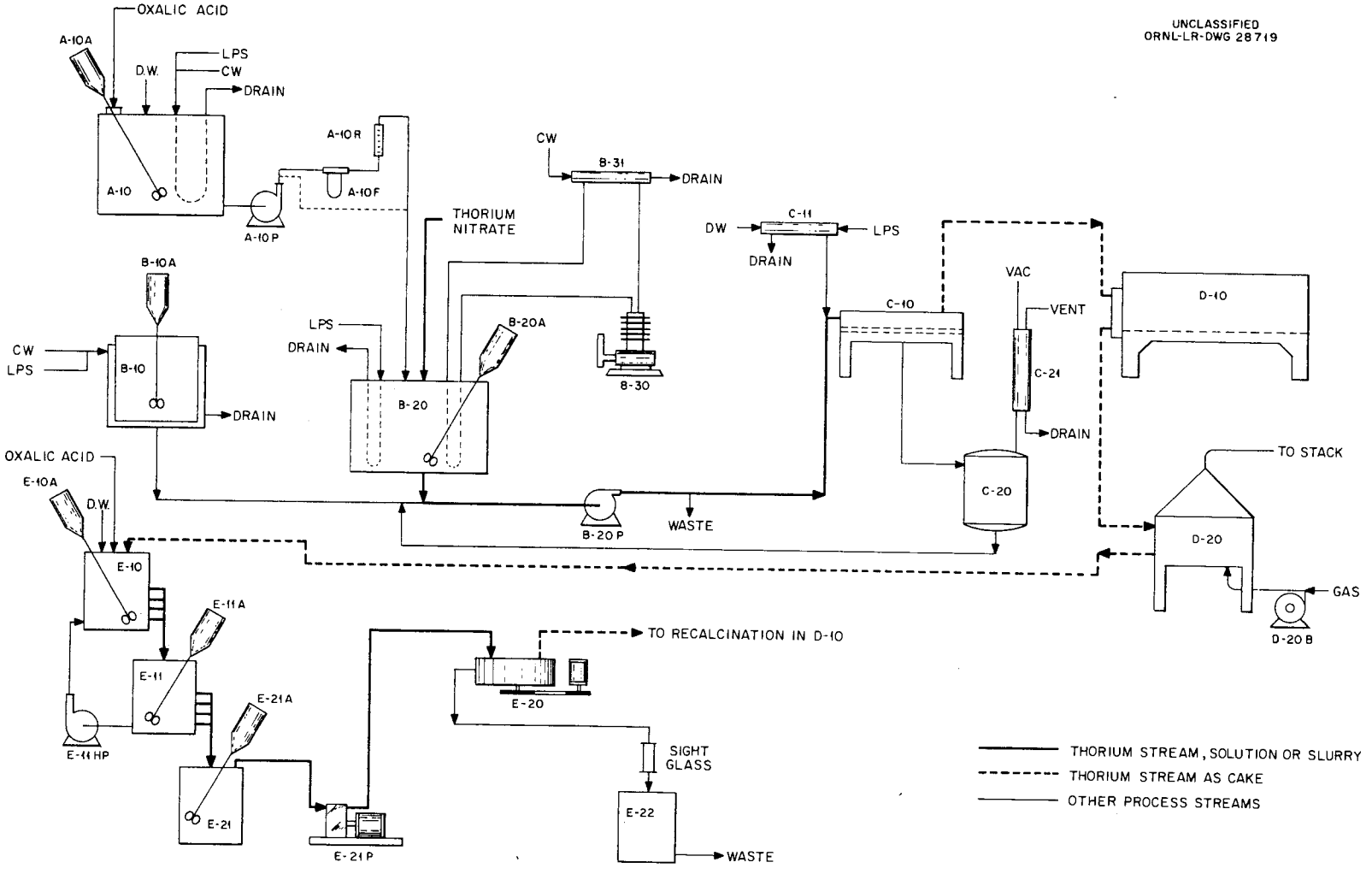

Fig. 3. Equipment Flowsheet for Thorium Oxide Preparation.

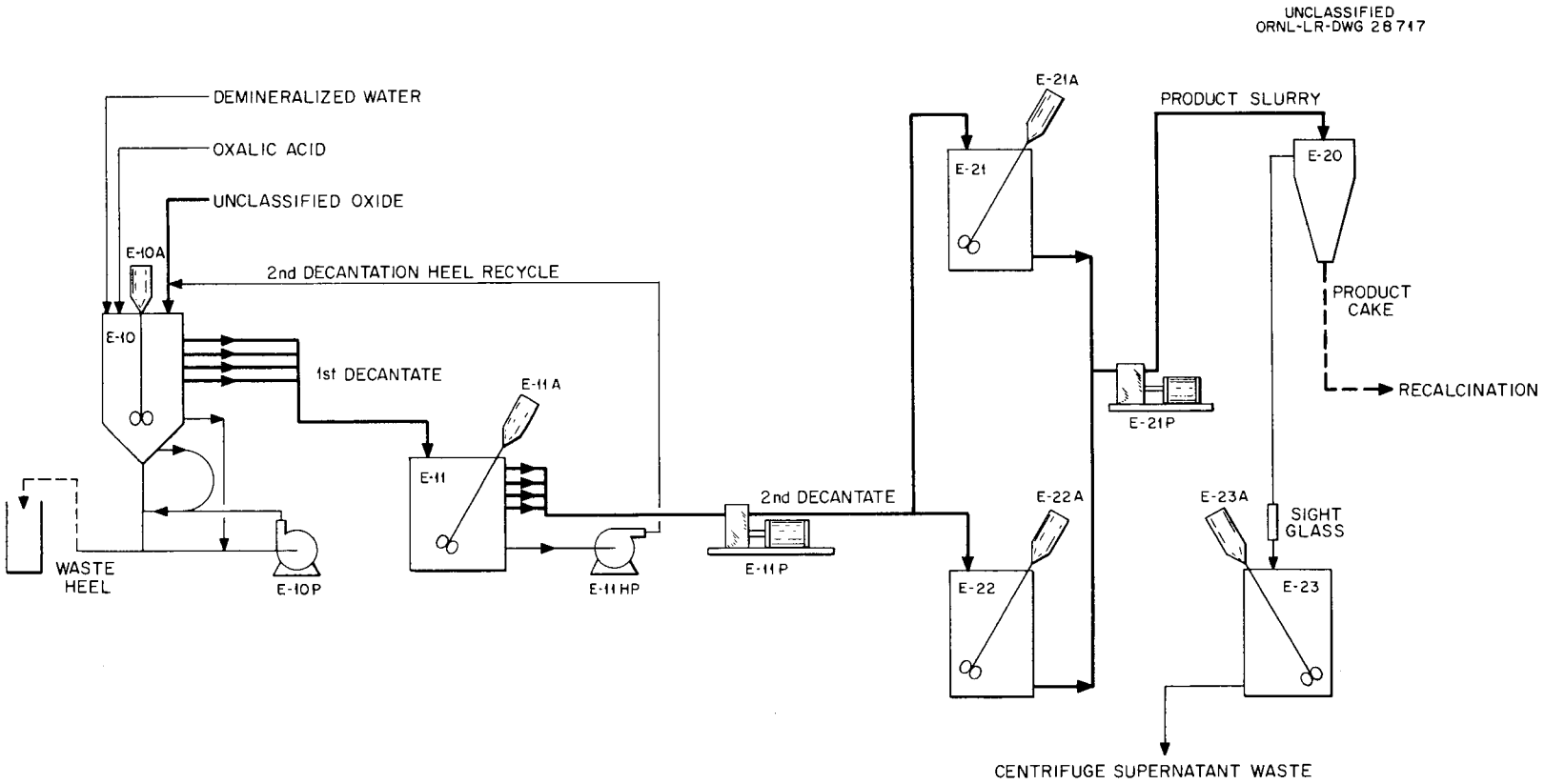

Fig. 4. Proposed Classification System.

The cake will be circulated into the agitator blades with a 5-hp 30-gpm Wilfley centrifugal slurry pump. The decantation tank, E-10, will be a standard 55-gal drum equipped with a 20-in.-deep cone bottom and with side drawoff lines spaced 6 in. apart for decantation. Supernatant from the second decantation tank, E-11, will be pumped to the product receiver tanks (E-21 and E-22) by a 0.5-hp 4.5-gpm Sigma Corporation finger pump. Heel from E-11 will be recycled to E-10 by a small portable Jabsco pump, eccentric flexible-impeller type (E-21 hp). The centrifuge will be an 1800-rpm (600, 700, and 800 G) American Tool and Machine Co. suspended-bowl separator (E-20) with a bowl 26 in. dia by 16 in. high (2.5 cu ft). Classified thorium oxide will be removed by an auxiliary motor-driven scraper.

2.3 Process Equipment Description

The principal equipment items are grouped into the precipitation, filtration, calcination, and classification systems. The material of construction for equipment in direct contact with the main process solutions and suspensions is stainless steel, principally of the 300 series. The major items of equipment are:

Precipitation System

Oxalic acid makeup tank (A-10): approximately 5 ft dia x 5 ft high cylinder; nominal capacity 600 gal

Oxalic acid pump (A-10P): 1.5-hp, 10-gpm Worthington centrifugal pump

Oxalic acid tank agitator (A-10A): 0.5-hp high-speed-propeller portable International Mixer

Oxalic acid filter (A-10F): 4 in. dia x 12 in. long glass wool element cartridge-type Fulflo Filter

Oxalic acid flowmeter (A-10R): 0-8.75-gpm Fischer and Porter rotameter

Precipitator tank 1 (B-10): approximately 2 ft dia x 6 ft high cylinder; nominal capacity 95 gal; tank equipped with cooling and heating jacket

Precipitator 1 agitator: 1-hp 285-rpm vertical Patterson Mixer

Precipitator tank 2 (B-20):* approximately 4 ft dia x 5 ft high cylinder nominal capacity 400 gal; tank equipped with cooling and heating coils

*The oxalic acid solution inlet of this tank has been a shower-bath type spray head, 8-pipe radial overhead sprinkler system, and is presently a draft-tube arrangement (Fig. 5). Oxalic acid solution is introduced inside the shell of the draft tube, mixed with the tank solution, and discharged at the bottom by the mixer. Most of the material produced between November 1957 and February 1958 was made with the radial perforated pipe distributor.

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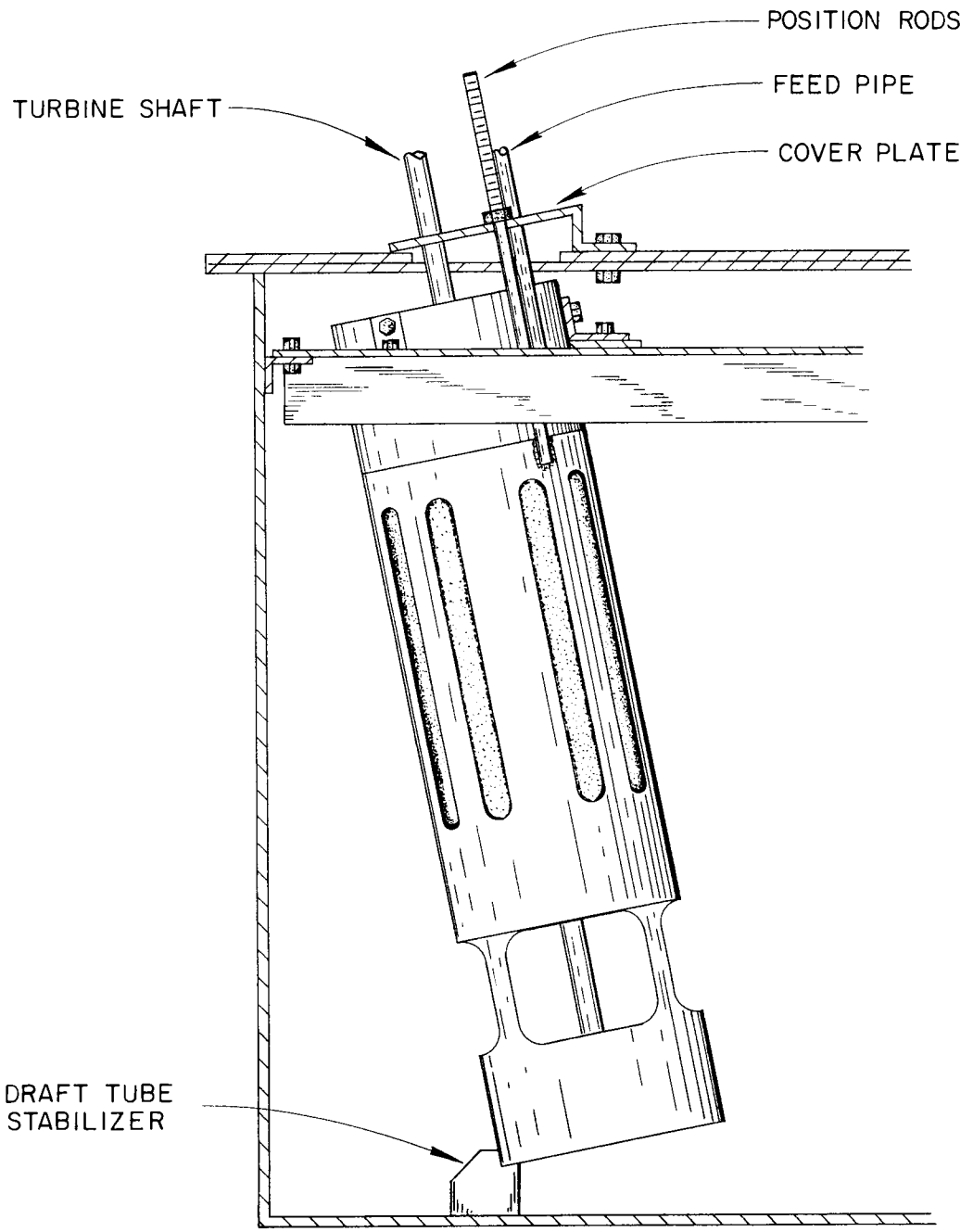

Fig. 5. Schematic Diagram of Draft Tube Installation.

Precipitator No. 2 Agitator (B-20A): 3-hp 433-rpm propeller-type inclined Lightnin (Mixing Equipment Company) mixer

Freon Compressor (B-30): 5-hp 180-psi piston-type Ice Machinery Corp. compressor with 20-in. Hg vacuum 180-psi Penn Corp. pressure controller

Freon condenser-cooler (B-31): type CRF-64 Bell and Gossett Corporation cooler

Precipitator No. 2 off-gas condenser (B-20C): 5-sq ft single-tube-pass Ross Heat Exchanger Corp. condenser

Filtration System

Filter (C-10): 4- x 4 ft open-bed vertical vacuum filter; filter medium, supported on a perforated (approximately 1/4-in.-dia holes) metal plate; cloth protected on top by 4-mesh metal screen; 12 in. freeboard above filter medium; filter vacuum is 10 in. water

Filter cloth: National Filter Media style 10 cotton duck and NS-1216 nylon have been used; dynel D-2001 has been obtained for future use to avoid deterioration in acid

Slurry transfer pump (B-20P): a low-head centrifugal pump

Vacuum receiver (C-20): approximately 2-ft-dia x 6-ft-long sealed cylinder. Nominal capacity 100 gal

Vacuum receiver sight glass (C-21): 3-in.-dia x 5 ft-long pyrex glass pipe mounted vertically between C-20 (bottom) and Bldg. 3019 vacuum supply (top)

Filter wash water heater (C-11)

Calcination System

Electric furnace (D-10): Trent Corporation muffle-type electric furnace, interior dimensions 4 ft long x 3 ft wide x 2 ft high; maximum operating temperature 1800°F; power rating 60 kw; steel rack in furnace carries 36 silica trays 16-3/4 in. long x 13-3/8 in. wide x 1-3/4 in. deep

Gas-fired furnace (D-20): R. C. Remmy Son Co. muffle-type natural gas-forced-air furnace; interior dimensions 25.5 in. long x 13 in. wide x 10 in. high; operating temperature 1600°C; thoria is fired in a covered rectangular platinum box 25 in. long x 6 in. wide x 3 in. deep; forced air is supplied by a 0.5-hp blower

Gas-fired furnace off-gas filter (D-21)

Classification System

First dispersion tank (E-10): standard 55-gal drum (22 in. dia x 34 in. deep); four supernatant drawoff tubes spaced 6 in. apart vertically up the side of the drum, starting 7 in. from the bottom; a 2-arm radial raker sweeps the bottom area of the tank with approximately 1/16 in. clearance

First dispersion tank agitator (E-10A): 0.25-hp high-speed-portable propeller Grenier and Co. mixer

Second dispersion tank (E-11): identical with first dispersion tank except that raker is omitted

Second dispersion tank agitator (E-11A): 0.5-hp high-speed-portable propeller Patterson Co. mixer

Product receiver tank (E-21): standard 55-gal drum

Product receiver agitator (E-21A): 0.25-hp high-speed-propeller portable Lightnin mixer

Product slurry pump (E-21P): 0.25-hp, 0.5 liter/min Sigma Corp. finger pump

Product recovery centrifuge (E-20): 1800-2000 rpm, 1/3-hp Tolhurst (American Machine and Metals Co.) centrifugal separator, bowl size 12 in. dia x 8 in. high

Centrifuge waste holding tank (E-22): standard 55-gal drum

3.0 PROCESS VARIABLES

3.1 Precipitation

The size and shape of the ThO_2 particle left after firing of the thorium oxalate to 650°C is a relic structure of the oxalate as it was formed.[1,2] It is therefore necessary to control the size and shape of the oxalate particles precipitated. In laboratory studies most of the precipitations were made with a direct strike,* which appeared to give an oxide product of smaller average particle size and fewer oversize particles than a reverse strike (Table 2). The fraction of oversize particles decreased with increasing

*Direct strike, oxalic acid solution into thorium nitrate solution; reverse strike, thorium nitrate solution into oxalic acid solution.

stirring rate and with decreasing mixing time. At a given temperature the uniformity of the product reached a maximum at a medium speed of agitation and was not changed by an increase in the stirring speed. With a direct-strike addition of reagent, the average particle size of the oxide product increased with increasing precipitation temperature, and more uniform products were produced at lower precipitation temperatures (Table 3). Decreasing the concentration of the two reagents increased the average particle size, but did not affect the size distribution (Table 4). The concentration of oxalic acid had more effect on the final average particle size than did the concentration of the thorium nitrate.

Table 2. Batch Thorium Oxalate Precipitation: Effect of Method of Adding Reagent, Agitation, and Mixing Time

Room temperature
1 M $H_2C_2O_4$: 1 M $Th(NO_3)_4$
Oxide product fired at 800°C

Solution Mixing Time, min	Particles in Excess of 5 μ, wt %					
	Direct Strike			Reverse Strike		
	18[a]	28[a]	38[a]	18[a]	28[a]	38[a]
6	5	3	2.5	13	5	9.5
5	4.5	6	2.5	14	13	5.5
4	5	3	1	8	3.5	1

[a]Stirrer speed in arbitrary units, settings on Brookfield counter-rotating mixer, model L-406.

Table 3. Batch Thorium Oxalate Precipitation: Effect of Precipitation Temperature

Direct strike
1 M $H_2C_2O_4$: 1 M $Th(NO_3)_4$
Stirring rate: 38 (see Table 1)
Mixing time: 4 min
Oxide product fired at 800°C

Precipitation Temperature, °C	Geometric Mean Particle Size (d_g), μ	Geometric Standard Deviation (σ_g)
10	0.88	1.36
20	1.02	1.39
30	1.20	1.45
40	1.25	1.62

Table 4. Batch Thorium Oxalate Precipitation: Effect of Reagent Concentration

Direct strike
Room temperature
Stirring rate: 38 (See Table 1)
Mixing time: 4 min
Oxide Product fired at 800°C

$Th(NO_3)_4$ Concentration, M	$H_2C_2O_4$ Concentration, M	Geometric Mean Particle Size (d_g), μ	Geometric Standard Deviation (σ_g)
0.5	0.5	2.77	1.37
	1.0	0.92	1.23
	1.5	0.67	1.37
1.0	0.5	1.85	1.39
	1.0	0.82	1.32
	1.5	0.76	1.35
1.5	0.5	1.98	1.36
	1.0	0.92	1.28

The reagents used in these studies were high-purity Lindsay Code 103 thorium nitrate and c.p. oxalic acid solution. The precipitations were made in a stainless steel beaker equipped with a Brookfield counter-rotating mixer, Model L-406. The geometry of the equipment roughly approximated the large-scale pilot plant production equipment. In direct-strike reagent addition, the oxalic acid was introduced under pressure into the thorium nitrate solution through a capillary tube projecting beneath the surface of the nitrate solution, the tube exit being directly above the agitator blades. The thorium oxalate precipitates were filtered immediately after the addition of the oxalic acid (addition time 2-24 min) and washed with water four times on the filter. The recovered precipitate was dried at 150°C and decomposed to oxide by a multistage calcination ending at 800°C. Particle size analyses were made by the improved neutron activation--sedimentation technique with sodium pyrophosphate dispersions in methanol, water, and glycerin-water mixtures.

It is common practice to present the particle size distribution in the form of a plot of the logarithm of the particle size versus the cumulative weight percent undersize on a scale based on the probability integral (Fig. 2). If the particle size data follow a logarithmic probability distribution (as it usually does with the ThO_2 preparations), the resulting plot is a straight line and the steeper the slope of the line, the less uniform the material.

The 50% size in such a plot is the geometric mean particle diameter (d_g). The geometric standard deviation (σ_g) is equal to the ratio of the 84.13% size to the 50% size (or of the 50% size to the 15.8% size).[3]

Draft Tube. Since both vigorous stirring and rapid addition of oxalic acid to thorium nitrate produced a product with little oversize material in it, precipitation was tried in a draft tube built around a downdraft agitator, with the oxalic acid entering inside the draft tube. The average particle size grew as the amount of recirculation increased (Table 5). The particles initially precipitated acted as nuclei, and the more times they circulated through the precipitation zone, the larger they grew. The final oxide had < 1 wt % oversize particles.

Table 5. Draft Tube Thorium Oxalate Precipitation: Effect of Recirculation Rate

Direct strike
1 M $H_2C_2O_4$; 1 M $Th(NO_3)_4$
Room temperature
Oxide product fired at 800°C

Recirculation Rate	Geometric Mean Particle Size (d_g), μ	
	6 min Mixing	4 min Mixing
Slow	0.99	0.99
Medium	1.42	0.91
Fast	2.48	1.30

3.2 Oxalate Digestion

Digestion of the thorium oxalate in its mother liquor overnight or raising the temperature of the oxalate slurry for several hours reduced sintering of the oxide at 1600°C. The earlier pilot plant oxides sintered to a greater degree, giving a product with over 30 wt % of the material over 5 μ.

3.3 Oxalate Filtration

The precipitated thorium oxalate is filtered and washed on a horizontal-bed batch vacuum filter. Several filter cloths gave acceptable filtration rates and low losses (< 2.0% ThO_2); a dynel cloth (National Filter Media Co. No. D-2001) was the most durable for the combination of nitric and oxalic acids. Cotton duck (National Filter Media Style 10) and nylon (National Filter Media NS-1216) were used, but both deteriorate in the acid.

3.4 Calcination

The final calcination of the ThO_2 is at 1600°C. The surface of this high-fired oxide is chemically less active than that of low-fired, and therefore the oxide adsorbs less fission and corrosion products. Its tendency to flocculate is less, and it is less friable. Because the gas-fired Remmey furnace available has only 2 cu ft capacity, the flowsheet includes a firing at 650°C, which reduces the oxalate volume 5-fold and thus increases the effective capacity of the gas-fired furnace.

For the final firing the oxide fired at 650°C is packed to half its bulk volume before the 1600°C firing. This packed material sinters to hard lumps when fired to 1600°C but is released in the classification step when the oxide is suspended in oxalic acid. Results of laboratory tests indicated that the chief effect of compressing the cake is to decrease the rate at which fines are released by the heel into suspension but that the ultimate yield is not affected seriously.

In a laboratory test ThO_2 (LO-36-800) was compressed to 54% of its original gross volume and fired at 1600°C for 4 hr. This material was hard and lumpy, while a control sample fired as dumped from an 800°C firing was loose and granular. Particle size analyses showed little difference between the two samples, despite the disparity in their gross physical properties. A test for oversize material also suggested little difference between the two samples. When 10-g samples of compressed and of uncompressed material were slurried separately in 100 ml of 0.003 M oxalic acid solution (pH 2.6), final yields of fines were slightly more than 50% for the compressed and slightly less than that for the control samples:

Slurry	Fines, g/10 g	
	Not Compressed	Compressed
Steeped overnight and then tumbled 30 min	1.75	1.10
Steeped 48 hr more and again tumbled 30 min	0.80	1.10
Tumbled 3 hr more	2.08	2.98
	4.63	5.18

In each case, 1 min was allowed for stilling before decantation, and the supernatant was decanted at a rate of 0.5 in./min.

Agitation during the steeping is essential, with less than 25% of the fines being released from uncompressed 150-g samples and only 3% from compressed after a week of steeping without agitation:

Slurry	Fines, g/10 g	
	Not Compressed	Compressed
Decanted immediately	0.72	0.30
Steeped 9 days without agitation	1.58	0.03
	2.30	0.33

3.5 Classification Product Concentration and Oxalate Removal

The ThO_2 is suspended in oxalic acid rather than water because ThO_2 flocculates badly. The recovered fines are separated from the oxalic acid by centrifuging and recalcining for 4 hr at 650°C. In a high centrifugal field ThO_2 flocculates and settles much more rapidly than would be expected from its particle size. It also forms a relatively firm, dense cake which is not easily removed hydraulically. Comparatively low-speed centrifuges and mechanical removal of the cake are therefore most satisfactory.

A Tolhurst laboratory centrifuge effectively concentrated Pilot Plant ThO_2 product at feed rates up to 0.5 liter/min with low losses:

Slurry Feed Rate, ml/min	Thorium Concentration, g/liter		ThO_2 Loss, %
	Feed	Overflow	
330	4.12	0.042	1.01
500	2.26	0.013	0.57
680	2.36	0.043	1.8
1140	2.13	0.047	2.2

The 12-in.-dia basket centrifuge operates at 2100 rpm to produce a centrifugal field of 750 G. A Sharples DV-2 centrifuge, which develops 6200 G, gave excellent separation at a feed rate of 2 gpm. However, in spite of the valves in its bowl which allow discharge of solids while the bowl is rotating solids could not be easily discharged and cleaning the unit after shutdown was difficult.

Attempts to remove the oxalate chemically were unsuccessful. Concentrated (30%) hydrogen peroxide rapidly decomposes concentrated oxalic acid to carbon dioxide and water at 50°C. However, the acidity of the dispersant is only 0.003 M, and dilute oxalate was not attacked by hydrogen peroxide. The slurry in this experiment, containing 100 g of 1600°C fired ThO_2 per liter, 0.005 M oxalic acid, and 2- to 10-fold excess hydrogen peroxide, stood as long as 5 days at 25, 50, and 100°C with no detectable decrease in the oxalic acid. Hydrogen peroxide is stable under the conditions of the tests. Results with formic acid, which is also a good dispersant for thoria, were similar. A 2-fold excess of hydrogen peroxide is sufficient to decompose completely the oxalic acid if the sample is evaporated to dryness at 90-100°C. No oxalate or peroxide was found in a thoria sample that was treated thus and then reslurried in an equal volume of distilled water and digested at 50°C for several hours.

Analysis for low concentrations of oxalate in the presence of higher concentrations of peroxide is complicated by the fact that most reagents that titrate oxalate also oxidize peroxide. The method followed in the above experiments was titration of the total oxidants in the sample with ceric sulfate as the oxidizing agent and determination of the peroxide by a starch-iodine method, assuming the difference to be due to oxalate. Formate cannot be determined by reduction of ceric sulfate.

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