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[illegible]

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THE LASL BISMUTH SULFATE THERMOCHEMICAL HYDROGEN CYCLE

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ABSTRACT

The LASL bismuth sulfate cycle is one of a generic class of solid sulfate cycles in which a metal sulfate is substituted for sulfuric acid in a hybrid (partly electrochemical) cycle. This technique avoids the serious materials and heat penalty problems associated with the handing of concentrated acid solutions, and if the electrolyzer is operated at acid concentrations below 50% it may, in principle, lead to a lower cell voltage with subsequent energy savings.

Experiment verification of all steps in the cycle has been obtained, particularly for the decomposition of normal bismuth sulfate and lower bismuth oxysulfates. For the substance, $Bi_2O_3.2SO_3$, an endothermic requirement of 172 kJ/mol was obtained, which is considerably less than that for other metal sulfate systems. A rotary kiln was used for continuous experiments and our results show decomposition of this compound to $Bi_2O_3.SO_3$ in under 8 minutes residence time at 1023 K.

Preliminary analysis of the cycle's energy balance shows an overall thermal efficiency of greater than 50% when the maximum cycle reaction temperature is 1500 K. The cycle has potential for hydrogen production when coupled with an energy source such as solar or fusion energy.

KEYWORDS

Hydrogen, thermochemical cycle, bismuth sulfate, hybrid cycle, efficiency, hydrogen production technology, solar energy, fusion.

INTRODUCTION

Thermochemical cycles for hydrogen production have been investigated at the Los Alamos Scientific Laboratory (LASL) since the early 1970's. These studies have consisted experimental and engineering research to define practical cycles that can be coupled with high-temperature heat sources for water-splitting to produce hydrogen and oxygen. In particular, the high-temperature energy sources surveyed were fusion and solar thermal energy.

Sponsorship of these programs has been obtained from the Department of Energy's (DOE) Divisions of Energy Storage Systems and Basic Energy Sciences. In recent months, our efforts have concentrated on the development of a hybrid (partly electrochemical) cycle that involves the decomposition of a solid sulfate as the high temperature step. Bismuth sulfate was the chosen sulfate for technical reasons which are detailed in a later section.

This paper addresses the rationale for introducing solids into a thermochemical cycle, specifics of the LASL cycle including the continuous decomposition of bismuth sulfate in a rotary kiln, and comments on the cycle efficiency and the cycle's adaptability to fusion and solar energy.

Development of Cycles Based on Solid Sulfate Decomposition

At present there are over thirty thermochemical cycles under differing degrees of research and development in laboratories around the world. Of these cycles, three have been selected for extensive development including the construction and operation of "closed-loop" demonstrator models that are capable of producing hydrogen continuously at 100 l/h rate. These three cycles and their developers are:

- The hybrid sulfur cycle (Westinghouse) (Parker, 1979)
- The sulfur-iodine cycle (General Atomic) (Besenbruch, 1979)
- The Mark 13 cycle, a sulfur-bromine cycle, (Joint Research Center, Ispra) (van Velzen, 1979)

Criteria used in the selection of these cycles include the use of an all-liquid or gas system, a maximum cycle temperature in the 1100 K range, and in two cases, the hybrid cycle and the Ispra Mark 13 cycle, the use of an electrochemical step for the low temperature hydrogen-producing reaction. All these cycles include evaporation of aqueous sulfuric acid solution, decomposition of sulfuric acid to water and sulfur trioxide followed by decomposition of sulfur trioxide to sulfur dioxide and oxygen as common steps.

The high-temperature step involving the handling and treatment of sulfuric acid and its components leads to severe materials problems in the area of corrosion which will require expensive materials of construction for resolution.

A possible means of overcoming the problems allied with the handling and decomposition of sulfuric acid lies in the introduction of a metal sulfate into the cycle (Bowman, 1974). This step is accomplished by contacting sulfuric acid produced by the low-temperature reaction with the appropriate metal oxide or metal oxysulfate to produce the desired sulfate species. Decomposition of the sulfate material then bypasses the corrosion problems associated with boiling sulfuric acid. However, containment of sulfur trioxide, sulfur dioxide and oxygen in the SO_3 reduction reactor at high temperature still remains.

It has been suggested (Bowman 1978) and there is now direct evidence (Remick and Foh, 1979; Parker, 1980) to indicate a reduction in electrolyzer voltage if the electrolyzer (for SO_2 oxidation) is at acid concentrations lower than 50 wt%, i.e., 10-30 wt%. At these concentrations, some metal sulfates are precipitated from their respective oxides or oxysulfates.

The major trade-off of this technique of introducing solid species into a previous all-liquid or gas cycle is solids handling. Associated with this problem is a drying problem. Typically, if the sulfate particles are small, acid solution is retained within the void space between the particles. Thermal energy must be applied to dry the solids and an effort must be made to recover the latent heat of the vapor, perhaps by recompression. (The authors have termed this the "laundry" problem for obvious reasons).

Other advantages and disadvantages of the solid sulfate substitution step are listed in Table 1

TABLE 1 Advantages & Disadvantages of Cycles Involving Solid Sulfates

Advantages

- Isothermal high-temperature operation possible - better thermodynamic match with fusion and solar energy sources
- Metal sulfates are less corrosive than sulfuric acid, materials selection easier
- Avoid heat penalties associated with the acid concentration step
- Lower operating voltage in hybrid cycles due to lower acid concentration in cell

Disadvantages

- Solids handling
  - Solids in pressurized systems
  - Heat transfer to/from solids
  - Sulfate/hydrogen mass ratio may be high
- Decomposition of sulfate may be slow as a result of kinetic or mass transfer limitations
- Sulfates need drying to remove occluded water, and waters of hydration must be removed
- Presence of metal cation may raise cell operating voltage in hybrid cycles

CHOICE OF METAL SULFATE SYSTEM

The bismuth sulfate system was chosen from among many competitive sulfate systems on the basis of the criteria listed below. In general, an "ideal" sulfate should possess the following characteristics:

- Low endothermic heat of decomposition
- Low or negligible solubility in acid solution
- Few or no waters of hydration present
- The decomposed material (oxide or oxysulfate) should easily combine with acid to form the starting material
- Low water retention for drying purposes
- Rapid decomposition kinetics at moderate temperatures
- Availability at low or moderate cost

In general the bismuth sulfate system selected fills many of the above criteria. Alternative sulfates have been selected by other workers in the field. Krikorian (1979) has suggested the use of zinc sulfate while Remick and Foh (1979) have chosen copper sulfate.

Table 2 is a compilation of the endothermic heats of reaction for several sulfate decompositions to form SO_2 and O_2. (Bowman, 1979) Clearly the bismuth sulfate system satisfies the first criterion decomposing at a relatively low temperature at around 1023 K. In addition bismuth sulfate is relatively insoluble, and normal bismuth sulfate, $Bi_2O_3.3SO_3$ is anhydrous. An alternative bismuth system based on bismuth oxysulfate, $Bi_2O_3.2SO_3$ has three waters of hydration. Both the zinc and copper sulfate systems form hydrates readily through some waters of hydration may be removed by raising the temperature of the acid solution. A final water of hydration does remain attached and must be removed prior to decomposition.

Favoring the bismuth sulfate system are low solubility, rapid reaction with sulfuric acid to obtain the desired sulfate or oxysulfate compound and fast decomposition at moderately high temperatures (ca. 1023 K). The water retention problem (approx. 10 moles of water are retained in the precipitate after filtration or centrifugation) needs further study for its resolution. Bismuth compounds are moderately expensive, (ca. $ 65/kg for reagent grade bismuth trioxide, Bi_2O_3), however this cost is included in plant inventory rather than in operating costs as recovery of all intermediate compounds in a thermochemical cycle is assumed.

In sum, it appears that the bismuth sulfate system is the logical choice as a solid sulfate alternative to sulfuric acid in thermochemical cycles.

THE LASL BISMUTH SULFATE CYCLE

A reference bismuth cycle has already been defined (Bowman, 1974; Cox, 1979) and it may be useful to review the chemistry of this cycle as an aid towards understanding the present version of the cycle. The reference cycle consists of the following steps:

$$2H_2O\ (l) + SO_2(g) = H_2SO_4(aq) + H_2(g) \quad \text{Elec.} \quad 350\ K \qquad [1]$$

$$H_2SO_4(aq) + 1/3\ Bi_2O_3(s) = 1/3Bi_2O_3.3SO_3(s) + H_2O\ (l) \quad 350\ K \qquad [2]$$

$$1/3Bi_2O_3.3SO_3(s) = 1/3Bi_2O_3(l) + SO_3(g) \quad 900\text{-}1200\ K \qquad [3]$$

$$SO_3(g) = SO_2(g) + 1/2O_2(g) \quad 900\text{-}1500\ K \qquad [4]$$

This cycle was originally devised as an alternative to cycles employing sulfuric acid and was used in a system study (Krakowski, 1979) that explored the concept of linking a fusion device to a thermochemical cycle for synfuel (hydrogen) production. A cycle temperature of 1500 K was used as the highest temperature capable of thermal delivery from the fusion blanket compatible with known materials. From the cycle's viewpoint, this temperature allows a higher degree of decomposition of the SO_3 gas in reaction [4] with the overall effect of raising the cycle's efficiency. Operation at a lower temperature more in keeping with temperature available from fission or solar thermal energy sources results in a lower yield for reaction [4] and a slightly lower value of the cycle efficiency.

In the reference cycle, the precipitated bismuth sulfate is normal bismuth sulfate, $Bi_2O_3.3SO_3$ or $Bi_2(SO_4)_3$.

The electrochemical oxidation of sulfur dioxide in water to produce hydrogen is the first step in this hybrid cycle. This reaction was first investigated by

TABLE 2 Sulfate Decomposition Data

	Reaction	ΔH^0_{298}(kJ)[a]	T (K)
1.	$BaSO_4 = BaO + SO_2 + 1/2O_2$	585	2025[b]
2.	$CaSO_4 = CaO + SO_2 + 1/2O_2$	510	1807[b]
3.	$MgSO_4 = MgO + SO_2 + 1/2O_2$	380	1329[b]
4.	$ZnSO_4 = ZnO + SO_2 + 1/2O_2$	334	1216[b]
5.	$CuSO_4 = CuO + SO_2 + 1/2O_2$	318	1118[b]
6.	$H_2SO_4(l) = H_2O(g) + SO_2 + 1/2O_2$	275	1125[c]
7.	$Bi_2O_3.2SO_3 = Bi_2O_3.SO_3 + SO_2 + 1/2O_2$	270	1023[d]

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a. (Bowman, 1979).
b. T calculated from $\Delta H^0_{298}/\Delta S^0_{298}$.
c. SO_3 is 80% decomposed at 1125 K.
d. Experimental data, this paper.

Bowman and Onstott (1974) at LASL. Subsequently, work on this reaction is still being performed at several laboratories as it is a key step in the cycle. A major consideration in this and other hybrid cycles is the reduction of cell voltage in the electrolyzer. Current goals are to achieve a voltage of less than 600 mV at a current density of 2000 A/m^2 in 50 wt% sulfuric acid.

The reference version of the LASL bismuth sulfate cycle was shelved for a number of technical reasons, among which were the formation of a liquid bismuth (tri-)oxide phase in the bismuth sulfate decomposer and electrolyzer operation at high acid concentration.

Cycle Variants

Variations in the reference bismuth sulfate cycle are possible because normal bismuth sulfate decomposes to a series of intermediate bismuth oxysulfates of lowering SO_3 content before reaching bismuth oxide, Bi_2O_3. The steps involved in the decomposition series are illustrated in Fig. 1 which also indicates the temperatures at which the decompositions take place. Also illustrated in Fig. 1 are the acid concentrations in equilibrium with the various species. Normal bismuth sulfate is stable in sulfuric acid solutions above 52.7 wt% (Urazov, 1958).

The apparently reliable work of Urazov (1958) also indicates that anhydrous $Bi_2O_3.2SO_3$ (or $Bi_2O(SO_4)_2$) is the stable phase in contact with H_2SO_4 solutions from 3 wt% to 52.7 wt%. Other work, deemed less reliable, has indicated the presence of hydrates. Recent work at LASL has shown that the trihydrate is formed in 1-3 M H_2SO_4. The trihydrate decomposes to a monohydrate at higher temperatures and eventually to the anhydrous compound. It may be possible to form the monohydrate by carrying out the reaction with sulfuric acid at sufficiently high temperatures.

The major purpose of Fig. 1 is to illustrate the concept that one can devise cycles by cycling back and forth between two intermediate species in the decomposition chain as long as the net result is the removal of 1 mol of SO_3 per mol of H_2 produced.

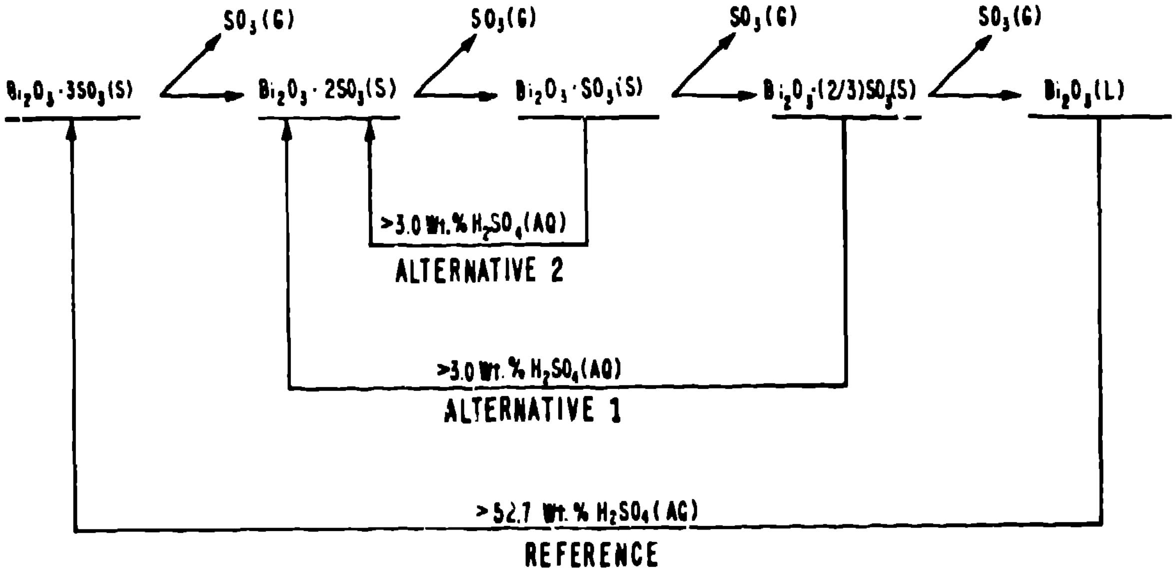

Fig. 1. Bismuth Sulfate Decomposition Alternatives.

An improved bismuth sulfate cycle would operate between the compounds, $Bi_2O_3.2SO_3$ and $Bi_2O_3.SO_3$ ($Bi_2O_2SO_4$). No liquids would be produced in the solids decomposition reactor, and low sulfuric acid concentrations giving lower values for the electrolyer cell voltage could thus be employed. As trade-offs, the $Bi_2O_3.2SO_3$ material produced as a precipitate would contain three waters of hydration, and more mass would have to be processed per mol of SO_3.

The present version of the LASL bismuth sulfate cycle follows:

$2H_2O(l) + SO_2(g) = H_2SO_4(aq) + H_2(g)$ Elec. 350 K [1]
$Bi_2O_3.SO_3(s) + H_2SO_4(aq) = Bi_2O_3.2SO_3(s) + H_2O(\ell)$ 350 K [5]
$Bi_2O_3.2SO_3(s) = Bi_2O_3.SO_3(s) + SO_3(g)$ 1100-1200 K [6]
$SO_3(g) = SO_2(g) + 1/2O_2(g)$ 1200+K [4]

The improved cycle is shown in schematic form in Fig. 2, data shows that the enthalpy change for reaction [6] above is only 172 kJ/mol SO_3 released. In contrast, the heat required for the complete transformation of normal bismuth sulfate to bismuth oxide requires 786 kJ/mol (Barin, 1977) or 262 kJ/mol SO_3 liberated.

Another alternative cycle shown in Fig. 1 could involve the decomposition of $Bi_2O_3.2SO_3$ to the compound $Bi_2O_3.0.7SO_3$.

Cycle Experimental Verification

The experimental evidence for the heats of decomposition in the bismuth sulfate system were obtained by Jones at LASL:

$Bi_2O_3.3SO_3(s) = Bi_2O_3.2SO_3(s) + SO_3(g)$ [7]
and, $Bi_2O_3.2SO_3(s) = Bi_2O_3.SO_3(s) + SO_3(g)$ [6]

The experiments were done in an isothermal batch apparatus and static gas pressures were obtained as a function of temperature. Straight line plots of log P(SO_3) vs. 1/T(K) gave a value of 161 kJ/mol for decomposition [7] and 172 kJ/mol for decomposition [6] respectively. These data and the experimental plots are shown in Fig. 3.

Kinetic data for the decompositions were obtained by dropping a holder containing a small sample (0.25 g) of $Bi_2O_3.3SO_3$ into a preheated furnace held at a set temperature. Measurements showed that the sample came to temperature equilibrium with the furnace temperature within 2 minutes. The SO_3 evolution rate is plotted as a function of time for runs at three different temperatures in Fig. 4. Less than two minutes time were required for the decomposition of $Bi_2O_3.3SO_3$ to $Bi_2O_3.SO_3$ at 1243 K. Less time (roughly half) is estimated for decomposition [6] above.

These results indicate that the reaction rate for the decomposition of bismuth sulfate or oxysulfate is determined by temperature-dependent kinetics rather than by heat transfer effects. In large industrial reactors, however, heat transfer to the solid particles will play an important role and this must be included in the design.

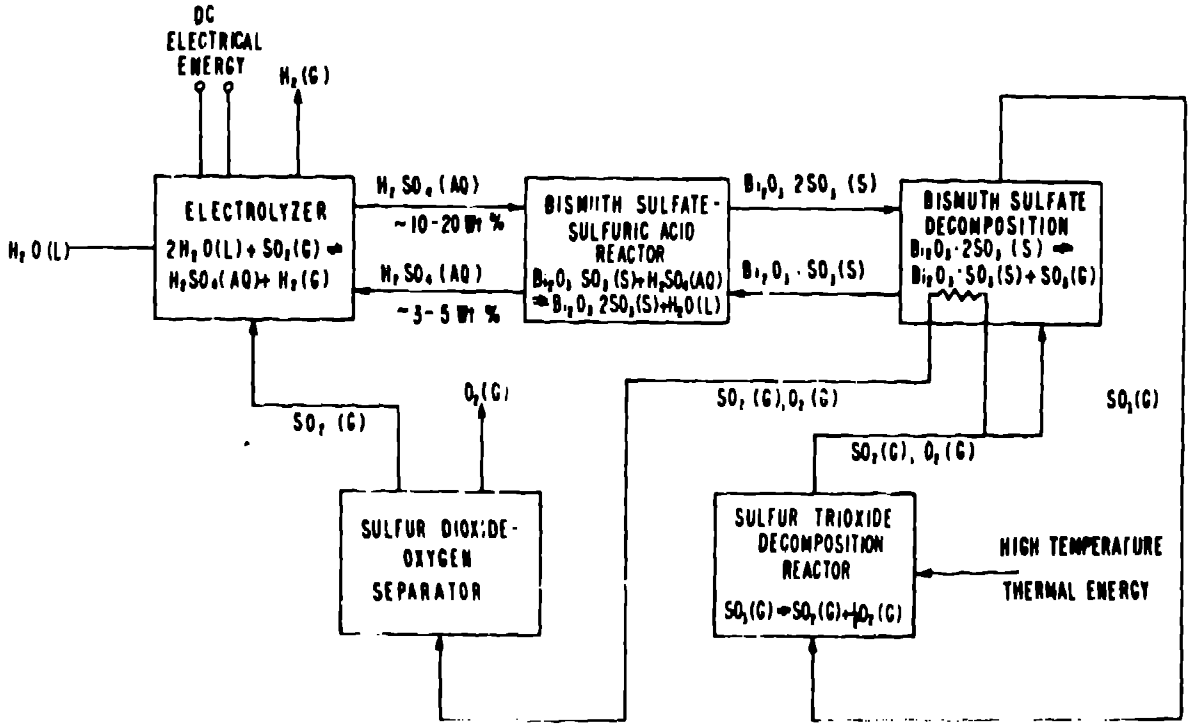

Fig. 2. The LASL Bismuth Sulfate Cycle - Schematic Diagram.

SOLIDS DECOMPOSITION FACILITY

A solids handling facility was set up to demonstrate the technical feasibility of the sulfate decomposition reaction in a continuous or flow mode and to show that recycled (decomposed) solids could be used over again in the cycle. The initial scheme tested involved the use of a fluidized bed solids/gas contacting scheme. The tests were run in a batch mode with an inert gas, nitrogen, as the fluidizing medium. Attempts at fluidizing the sulfate particles made by our first preparation were unsuccessful. Examination of the morphology of these particles under an optical microscope (and later by Scanning Electron Microscopy, SEM) showed them to be highly acicular with aspect ratios varying from 7-10. On in-

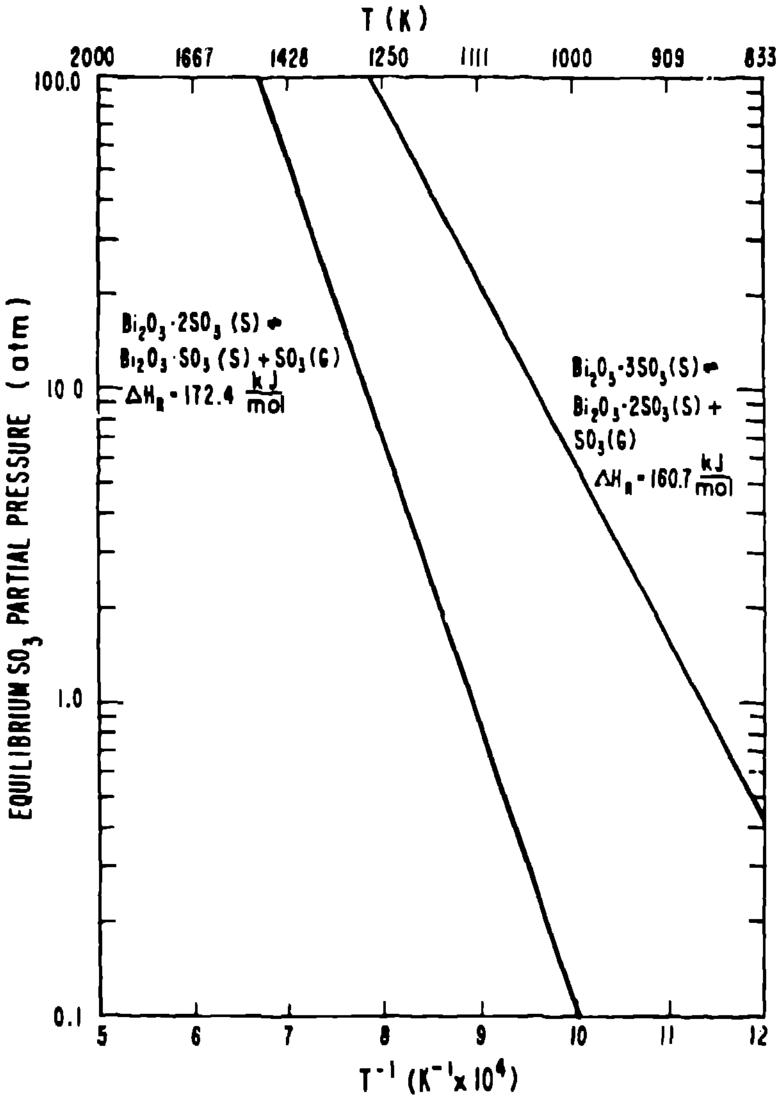

Fig. 3. Decomposition Pressures for $Bi_2O_3.3SO_3$ and $Bi_2O_3.2SO_3$

troduction of the fluidizing gas, the bed of particles would tumble and the particles would roll into larger spherical masses or "pills." The sulfate particles appeared to interlock rather than behave as individual elements. As a result of this behavior, the fluidization experiments were shelved in favor of a more general solids decomposition scheme practiced widely in industry for processes such as roasting, calcination, etc. This scheme uses a rotary kiln as the solids handling device.

Rotary Kiln

A bench-scale rotary kiln was constructed from a 25 mm dia. quartz tube 1.5 m in length. The overall kiln is shown in Fig. 5. At the head or "feed" end of the kiln, the quartz tube was fitted into a screw feeder made by inserting a Teflon screw in a tapered Teflon plug. A more detailed view of the "feeder" arrangement can be seen in Fig. 6. A Vee-shaped hopper was used for feed material storage, and the whole device was attached to the top of a vibratory device to aid in moving the solid particles. A key feature in the design of the plug was to allow rotary motion of the kiln and yet provide a gas seal. The seal was important as we wished to recover the gases evolved from the decomposing solids (sulfur tri-

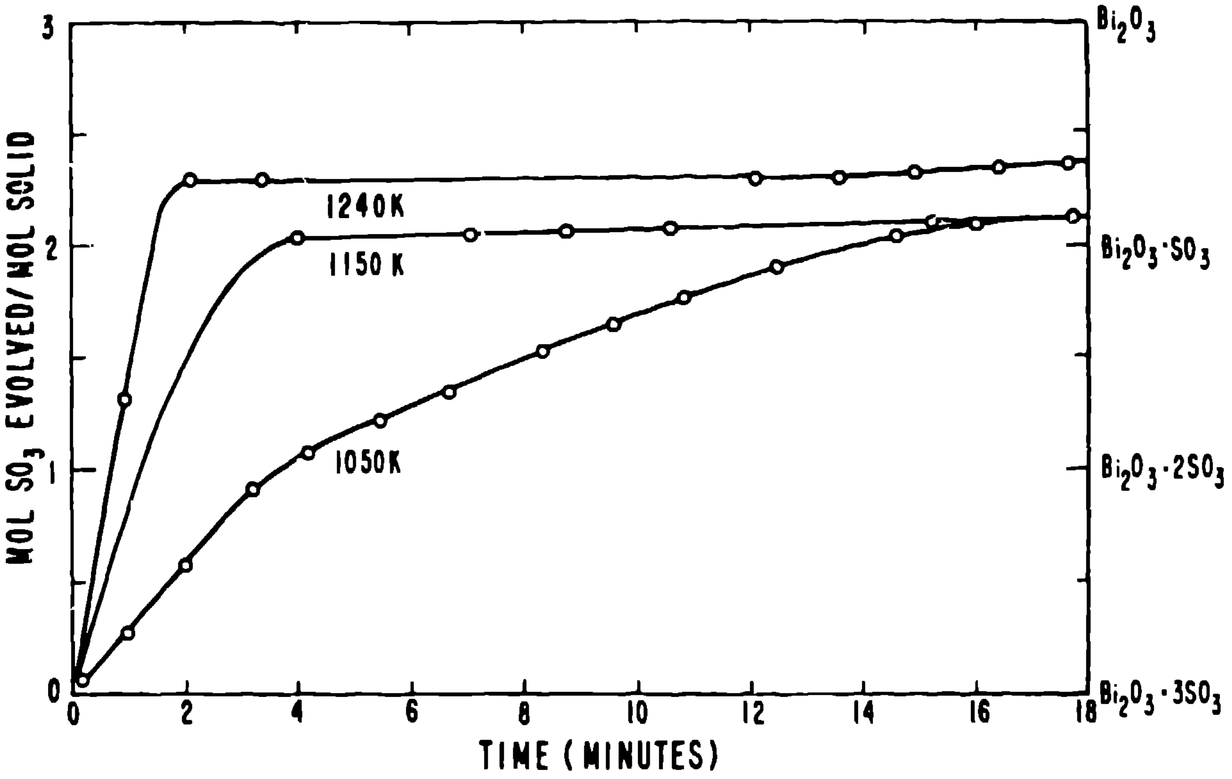

Fig. 4. Kinetics of $Bi_2O_3.3SO_3$ Decomposition.

oxide) as well as provide a controlled atmosphere inside the kiln and keep moisture out. The Teflon plug was fitted to a standard taper-joint on the end of the quartz tube.

A tubular furnace enclosed the center portion of the kiln tube. This enclosed length, 33 cm in length was the working kiln. The furnace temperature could be set to a desired temperature for a decomposition run. Passage of material through the heated kiln can be seen in Fig. 7. In this figure, the upper portion of the furnace has been momentarily raised to show the sulfate particles passing downwards through the quartz tube section. The downstream or collection end of the kiln apparatus is shown in Fig. 8. A flask-shaped device added to the end of the tube performed this function. Two glass vials 180 degrees apart were the sample removal ports for the decomposed product. An electric motor geared through a drive mechanism rotated the kiln by a chain-sprocket attached to the quartz tube. The speed of kiln rotation could be varied by this arrangement. The whole mechanism was mounted on a metal chassis that could be lowered or raised by means of elevating screws at the "feed" end of the kiln. This allowed for variable slope. Not shown in Fig. 8 is a small rotary seal fitted to the downstream end of the tube that allowed for the introduction of an inert gas to sweep away the gaseous decomposition products. A gas absorber tube filled with Ascarite was sometimes used to collect the sulfur trioxide formed, on other occassions this gas was vented to the fume hood enclosing the entire bench-scale kiln.

Feed Preparation

Prior to running experiments in the kiln, it was necesssary to define a procedure that would provide a uniform feed material - both as regards feed composition and morphology (particle shape and size). The starting bismuth sulfate was initially prepared from bismuth trioxide reagent grade chemical, as recycle (decomposed sulfate) was unavailable. Two differing methods were used in the preparation of the

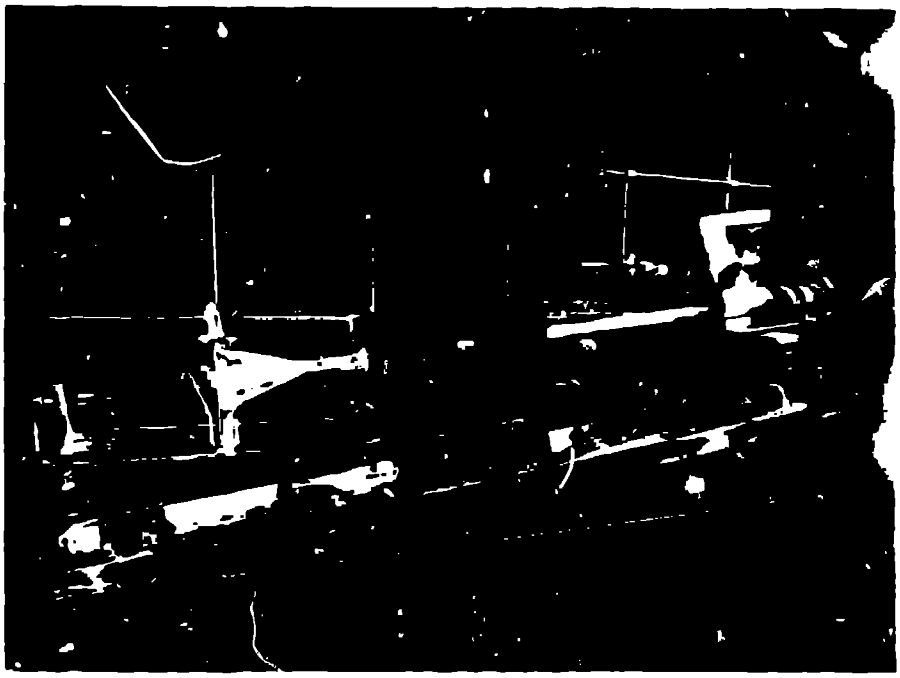

Fig. 5. Rotary Kiln for Bismuth Sulfate Decomposition.

feed sulfate.

Preparation Method 1

In this preparation, bismuth oxide reagent was slowly added to a stirred sulfuric acid solution of known concentration to yield a given weight of product as well as a final acid concentration. The precipitated sulfate was filtered, washed to remove acid, and dried overnight at 623 K (350 C). This method produced the acicular shaped particles used in the initial fluidization experiments. These were needle-like and had the approximate dimensions, < 1 μ dia. by 5-10 μ long when undigested as determined by SEM photomicrographs. Water retention by this material was large and in excess of 10 mols of water/mol of sulfate due to the high void volume present. This method of preparation produced a material with a stoichiometric formula close to $Bi_2O_3.2SO_3$. The particles, in addition to not being easy to fluidize, also prove very difficult to feed in the screw feeder. Packing of the particles caused bridging and plug-up of the feeder even with the use of the vibratory shaker. In fact, the vibratory motion sometimes made matters worse in further compacting the particles. It was therefore necessary to devise a new method of feed preparation to alleviate this problem.

Preparation Method 2

This method of preparation successfully resolved the above difficulties. It consists of adding sulfuric acid of known strength to an aqueous slurry of bismuth oxide particles, the slurry was kept at close to the boiling point of the liquid (363-373 K) and a period of digestion (stirring) was allowed for particle growth to occur. Results of the second preparation method are seen in Table 3. High bismuth sulfate yields were obtained in all cases well within the experimental

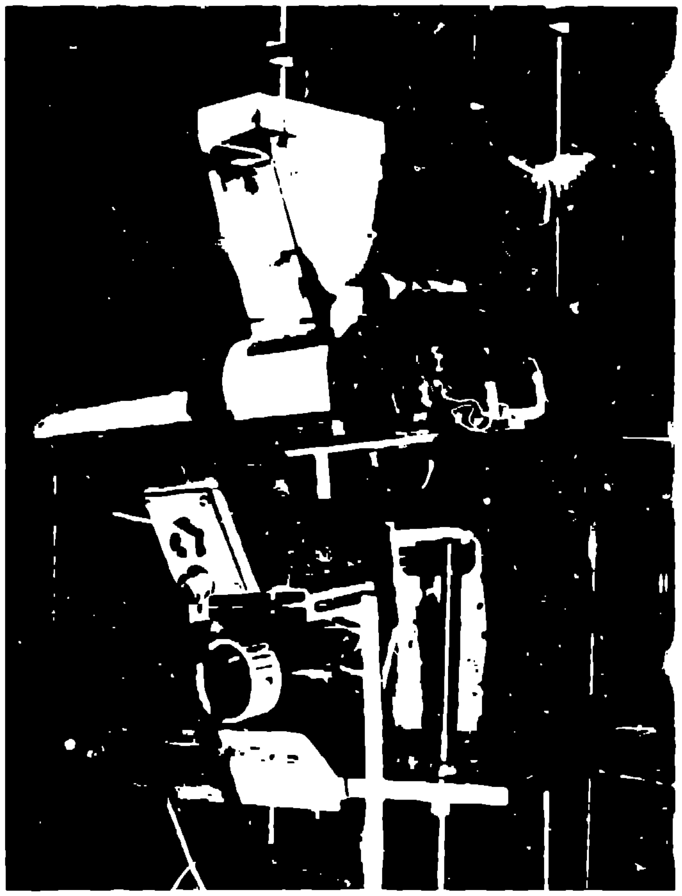

Fig. 6. Solids Feeder for Rotary Kiln.

error of the experiments. The rise in stoichiometric product composition is due to a further processing change between the two preparation methods. As washing would not be an integral feature of the final process flowsheet, drying of the wet filter cake was performed without the latter operation. On drying, the acid present in the occluded liquid concentrates and further reacts with the originally precipitated $Bi_2O_3.2SO_3$ to give a mixture of this material and some $Bi_2O_3.3SO_3$ represented by the product compositions shown in Table 3. Bulk density tests were also carried out to help characterize the feed material. The higher the bulk density of the sample, the lower the void fraction indicating that the particles in the sample possess a more uniform shape. The tap density value reflects the density of the particles after 5000 taps. It is another indication of the particles' morphology. The major disadvantage noted in these preparation runs was the amount of liquid retained (occluded solution by the product which approximated 10 mols of water per mol of dry product. All material prepared by the second method proved easy to feed.

Kiln Operation

The key variables affecting the operation of a kiln in which solid species undergo decomposition are:

TABLE 3. Preparation of Bismuth Oxysulfate Feed (Method 2)

Run	A	B	C	D
Initial Acid Conc. (M)	4.0	4.0	4.0	4.0
Final Acid Conc. (M)	2.59	1.84	2.57	2.59
Digestion Time (h)	1.5	1	1	1
Digestion Time (C)	87	96	97	97
Sulfate Composition	$Bi_2O_3.2.16SO_3$	$Bi_2O_3.2.14SO_3$	$Bi_2O_3.2.45SO_3$	$Bi_2O_3.2.07SO_3$
Yield (%)	97.7	98.6	97.9	97.5
Mol. H_2O/Mol. Product*	9.75	9.24	13.1	9.98
Bulk Density (g/cm^3)	1.03	1.00	1.29	1.15
Tap Density (g/cm^3)	1.90	1.58	1.99	1.78

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*In filter cake

- o Solids residence time - a function of:
  - kiln length and diameter
  - kiln rotation speed
  - kiln slope

o Kiln operating temperature. An empirical equation linking the residence time to the major dependent variables is given by (Perry, 1977):

$$\theta = \frac{0.19\ L}{NDS}\text{ , where,}$$

θ = time of passage in kiln (min)
L = kiln length (m)
N = rotational speed, (rpm)
S = slope of kiln (m/m)
D = kiln diameter (m)

The time of passage for the particles can also be roughly ascertained by visual observation of a "front" of particles as it passes over a given distance. To date, we have set the kiln temperature at a constant 1023 K (750 C) as well as the kiln diameter (25 mm) and length (33 cm). The major variables therefore affecting the solids residence time are the kiln's pitch and rotational speed.

Table 4 shows preliminary results on the kiln's operation that indicate close correlation with the previously mentioned batch decomposition results. The decomposition is fairly rapid and residence times of 8 minutes at 1023 K give the desired result, i.e., a mol of SO_3/per mol of entering feed sulfate.

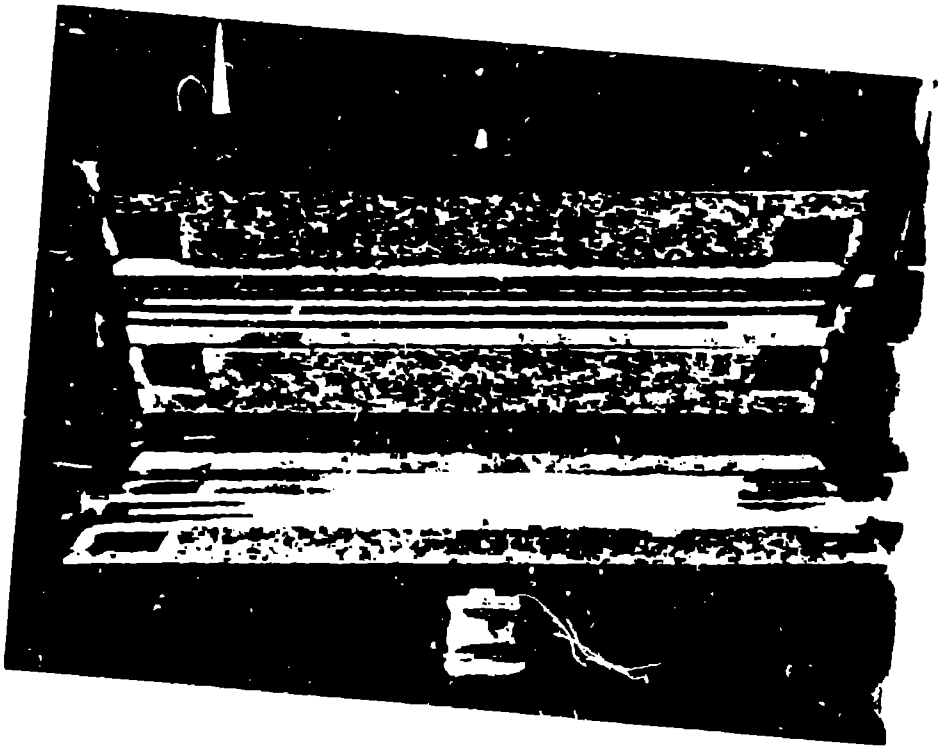


Fig. 7. Passage of Solids Through Rotary Kiln

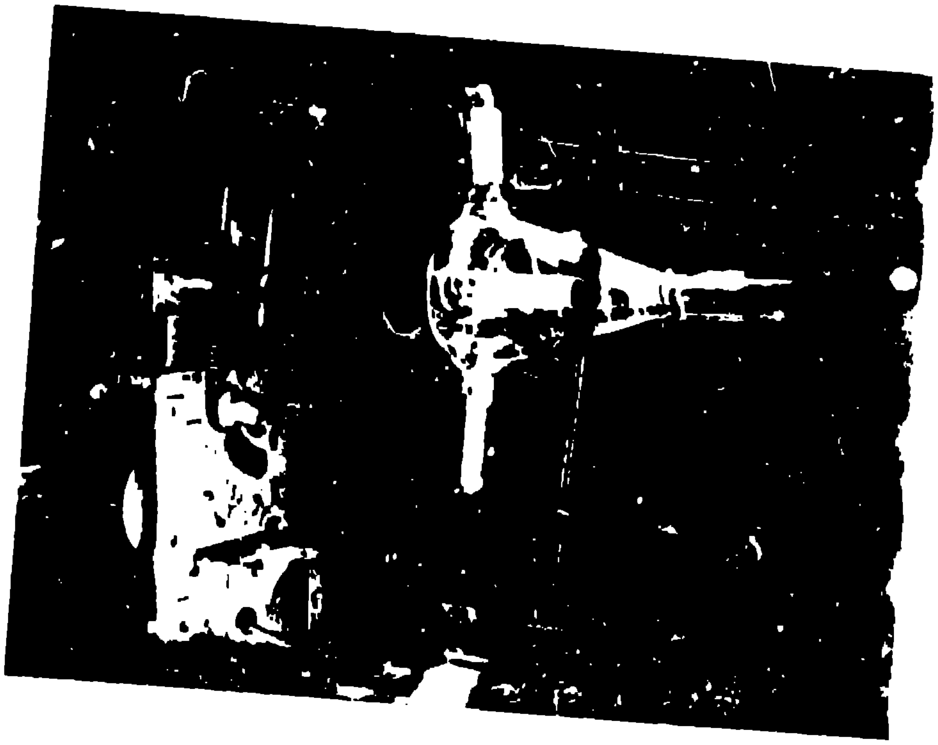


Fig. 8. Rotary Kiln Collection End

Table 4. Decomposition of Bismuth Oxysulfate in a Rotary Kiln

Run	Feed Composition	Product Composition	Prep. Method	T (K)	Residence Time (min)
1	$Bi_2O_3.1.90SO_3$	$Bi_2O_3.0.72SO_3$	1	1023	20
2	$Bi_2O_3.2.98SO_3$	$Bi_2O_3.1.92SO_3$	2	1023	8
3	$Bi_2O_3.2.07SO_3$	$Bi_2O_3.1.07SO_3$	2	1023	8
4	$Bi_2O_3.2.14SO_3$	$Bi_2O_3.1.55SO_2$	2	1023	3
5	$Bi_2O_3.2.16SO_3$	$Bi_2O_3.1.64SO_3$	2	1023	2.5

In run 5, decreasing the residence time to 2.5 min. brought about the release of only 0.52 mols of SO_3 per mol of entering feed which corresponds to roughly 50% of the desired conversion at 1023 K.

BISMUTH SULFATE MORPHOLOGY

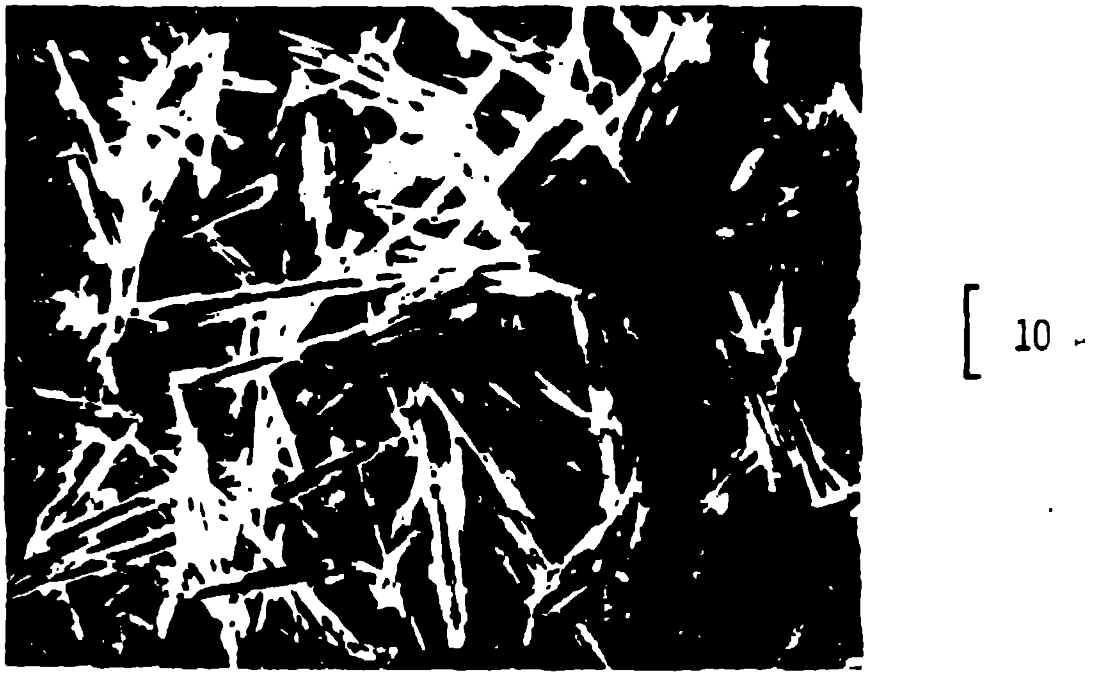
A study of the morphology of the particles formed in the two methods of preparation and after passage through the kiln has been initiated. Samples of the bismuth oxysulfate preparations were viewed on the SEM and photomicrographs of representative particles were taken. Material prepared by the first method is shown in Fig. 9. These particles have acicular shapes and dimensions corresponding to 1 μ dia. by 5-10 μ long. The decomposed material from this preparation is also seen in Fig. 9 and appears to have the same overall dimensions as before, however the particles are rounded off. Some of the decomposed particulate material appear to have been sintered indicating the possibility of the liquid phase of Bi_2O_3 being present during the decomposition process.

Material prepared by the second method is shown in Fig. 10 together with its decomposed counterpart. The feed material is much less acicular than material prepared by the first method (Fig. 9). These particles are no longer needle-like but much more uniformly sized. The decomposed material is similar in shape and size to the starting material.

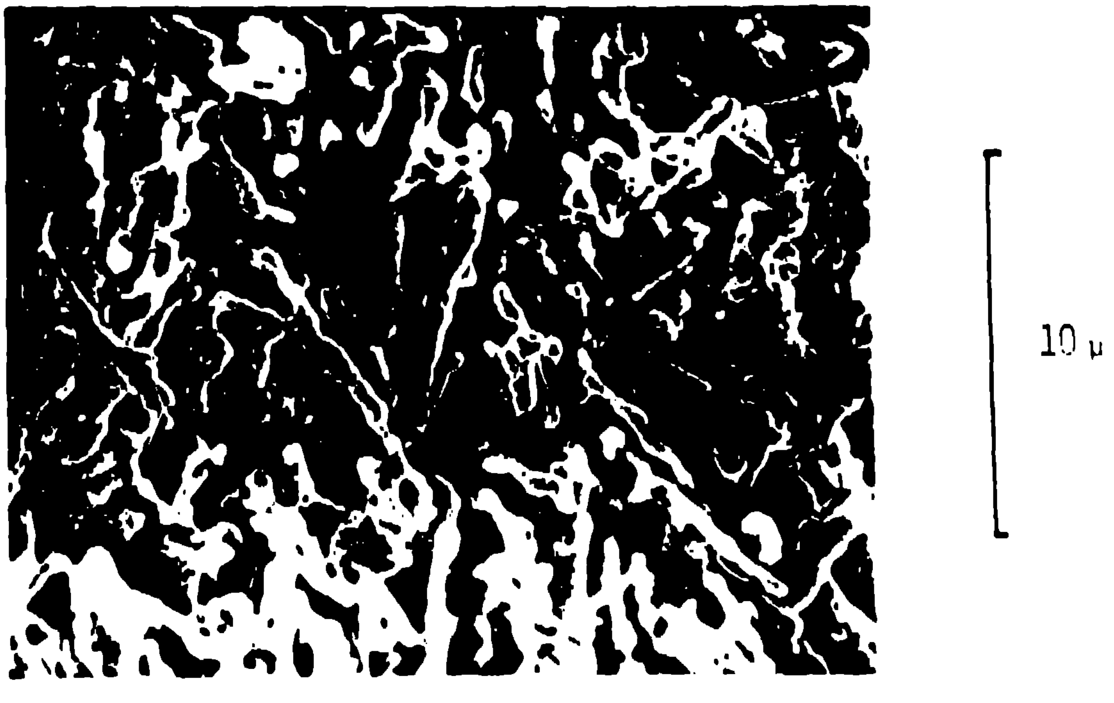
We conclude that the decomposition process does little to destroy that morphology of the starting material fed to the kiln. Later work will be done to determine the morphology of the recycle oxysulfate particles made by contacting the decomposed material with sulfuric acid.

PROCESS DESIGN

A thermochemical process design has been done for the reference and improved versions of the LASL bismuth sulfate cycle. The design goals were to produce an engineering flowsheet, compute mass and energy balances, and obtain a value for the overall thermal efficiency of the cycle. In this conceptual design, the energy source under consideration was a fusion reactor that contained a high-temperature boiling lithium blanket as part of the design. This blanket transferred heat directly to a $SO_3/SO_2/O_2$ process stream for the high-temperature (1500 K) portion of the cycle. Heat from a lower temperature portion (800 K) provided the energy for electricity generation to power the SO_2 electrolyzer units. The details of this study are included elsewhere (Cox, 1979; Cox, 1978; Krakowski, 1979).

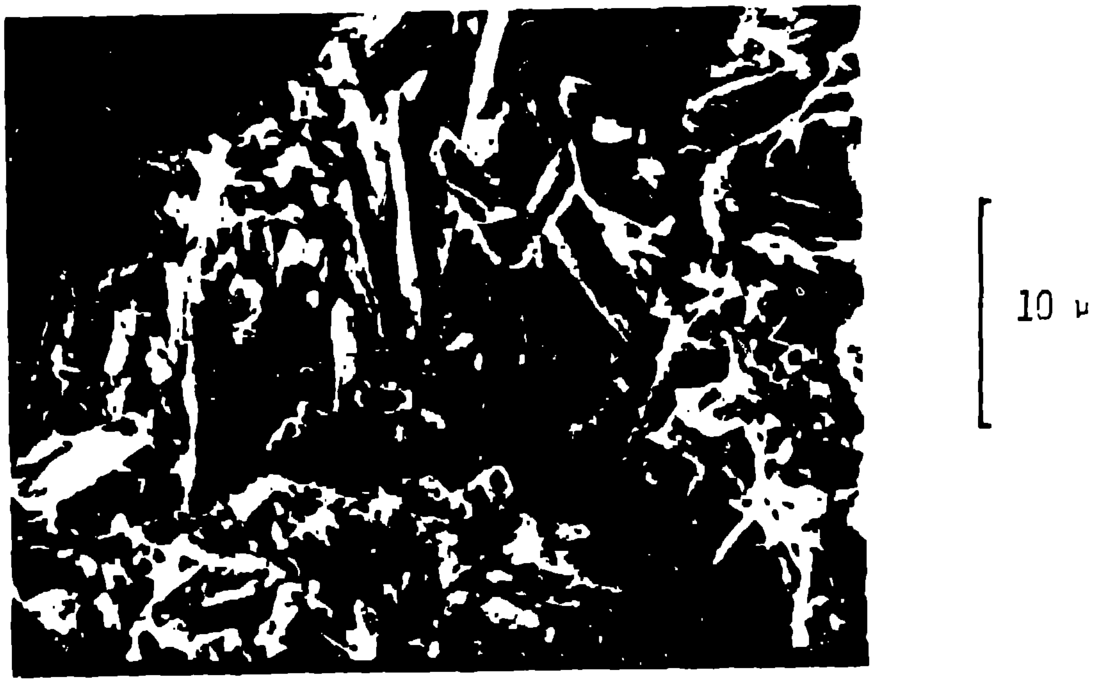


$Bi_2O_3 \cdot 2.02SO_3$ - FEED

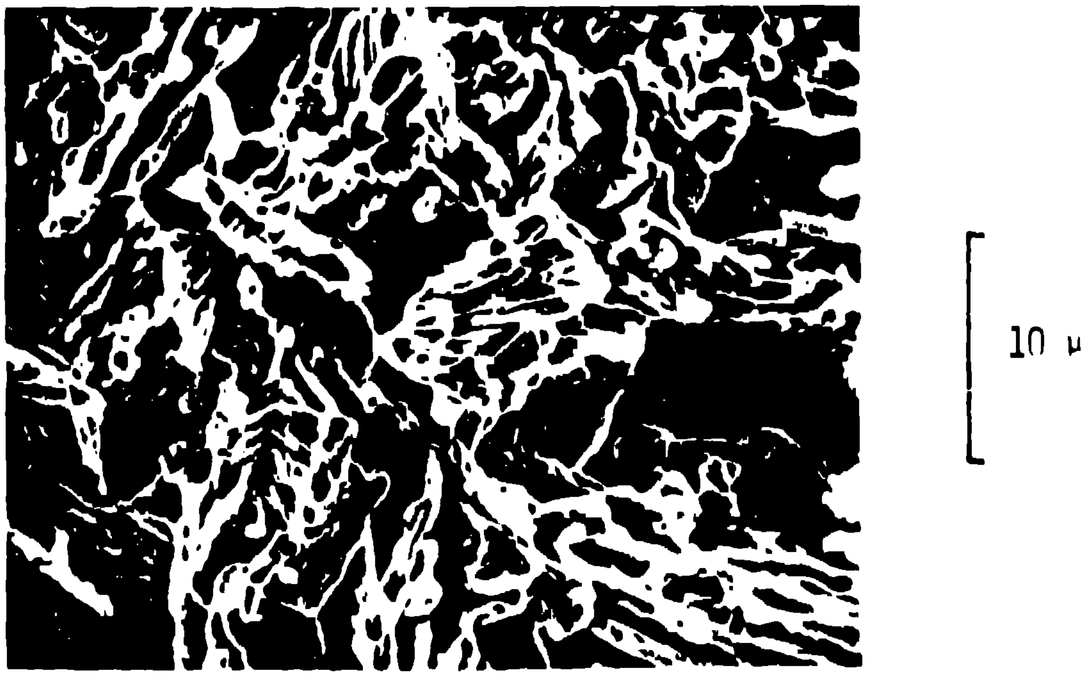


$Bi_2O_3 \cdot 0.72SO_3$ - PRODUCT

Fig. 9. $Bi_2O_3 . 2SO_3$ - Preparation Method 1. Kiln Feed and Product.



$Bi_2O_3 \cdot 2.07SO_3$ - FEED



$Bi_2O_3 \cdot 1.07SO_3$ - PRODUCT

Fig. 10. $Bi_2O_3.2SO_3$ - Preparation Method 2. Kiln Feed and Product

Energy Balance and Efficiency Calculation

The energy balance for the cycle will be reviewed as it has a direct bearing on the applicability of the LASL cycle for fusion or solar high-temperature heat sources.

The cycle energy balance is illustrated in Fig. 11. The cycle is split into two portions, a high-temperature portion and a low-temperature portion. Included in the high-temperature portion are batteries that perform the following functions:

Battery	Function
A	Solids Dewatering (Drying)
B	Solids Decomposition
C	SO_3 Decomposition

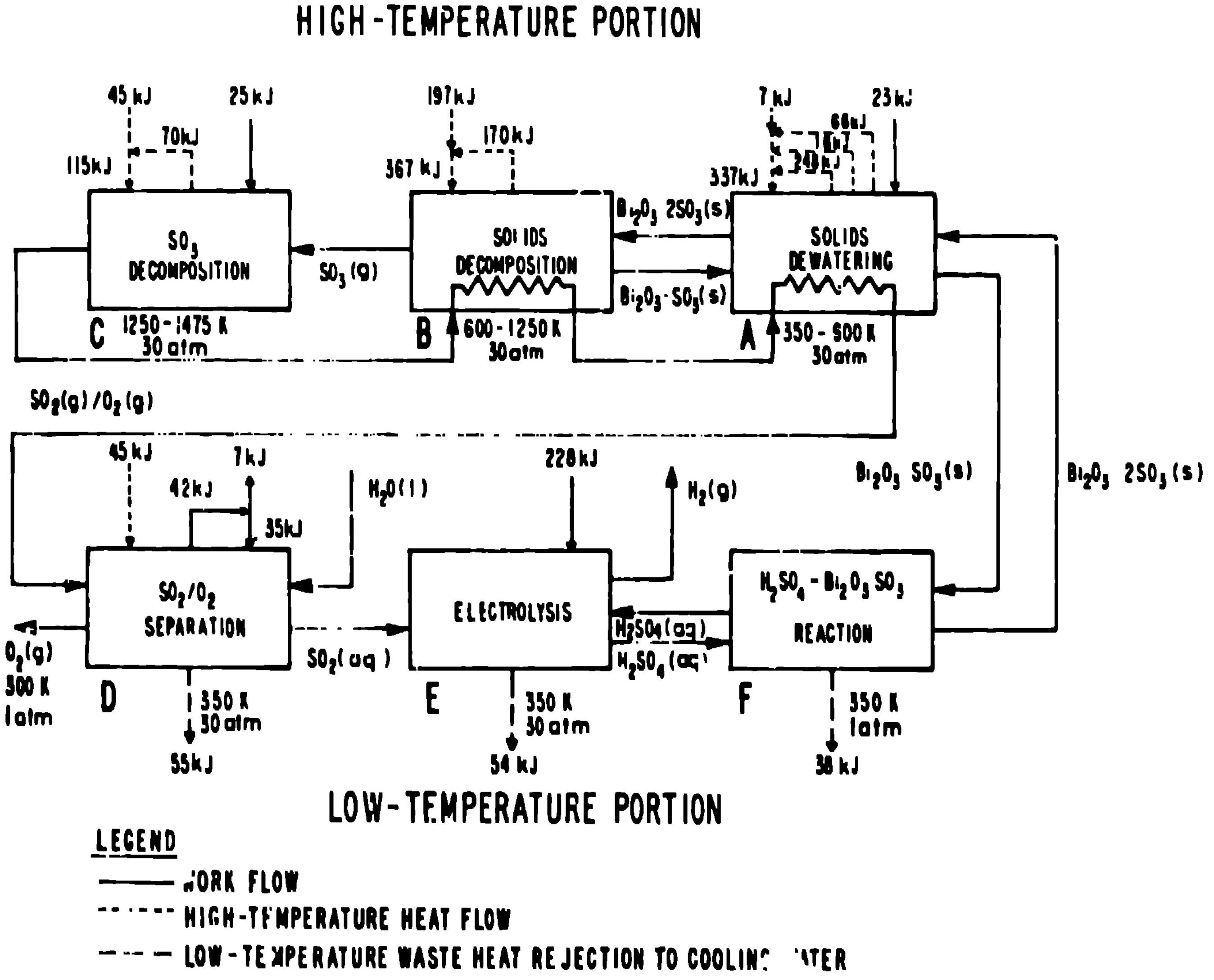


Fig. 11. Overall Energy Balance Diagram for the LASL Bismuth Sulfate Cycle.

The main function of Battery A, Solids Dewatering, is to dry the incoming $Bi_2O_3 \cdot 2SO_3$ solids and to recover as much heat as possible from heated streams and the latent heat present in the vaporized water. The gross heat duty of this unit is 337 kJ/mol hydrogen (All heat values were based on 1 mol hydrogen produced by the cycle). By use of a vapor recompression device consuming a thermal equivalent of work equal to 23 kJ, it is possible to recover 248 kJ of energy for a net usage of only 112 kJ. In this calculation, we assumed that only 5 mols of water entered per mol of solid.

Battery B is equivalent to the rotary kiln in our recent experiments. In our process design, a novel "chemical heat pipe" mechanism was used to transfer heat for the decomposition process. In battery C, SO_3 is almost completely decomposed to SO_2 and O_2 at 1500 K, this gas mixture is passed over the bismuth solids held at a lower temperature thus shifting the equilibrium of the gases to producing more SO_2 and O_2 releasing of thermal energy for the solids decomposition endothermic demand. In this manner, heat transfer through a solid wall to a particulate solid phase is avoided and only a gas wall heat exchanger, albeit a high-temperature heat exchanger, is required.

The low-temperature portion of the cycle is comprised of batteries D, E, and F. SO_2 is separated from O_2 by gas absorption in battery D, a standard chemical engineering technique practised in industry. Electrolysis is carried out in battery E under the following assumed conditions:

Electrolyzer operating voltage: 450 mV
Current density: 2000 A/m^2
Acid concentration: 15 wt%
Temperature: 350 K
Pressure: 30 atm.

The above data reflect optimum as regards the cell voltage. An acid concentration of 25 - 30 wt% may be better for cell operation as the acid resistance is less at these concentrations. A parametric analysis performed with cell voltage as a major variable indicated a drop in cycle efficiency of 1% for each 20 mV rise in cell voltage. Battery F consists of the slurry reactors in which the decomposed solids are regenerated with fresh acid from the electrolyzers, battery E. This reaction has an exothermic heat estimated at 38 kJ/mol based on measured values by Jones at LASL for the formation of normal bismuth sulfate from bismuth oxide and sulfuric acid.

Overall Efficiency of Cycle

The cycle's efficiency was computed from the values presented in Fig. 11. The net heat requirement (heat plus thermal equivalent of all work input) was 563 kJ giving an efficiency value for the cycle of 286/563 = 0.508 (50.8%) under the conditions specified in the process design. Three variables were selected for a parametric analysis on the cycle efficiency. These variables were: the cycle electrolyzer voltage which has already been discussed, the maximum cycle temperature, and the endothermic heat requirement in the high-temperature portion of the cycle. The effect of maximum temperature is important as this temperature affects the equilibrium yield in the SO_3 decomposition equilibrium reaction, and thus the composition of the gas phase in batteries B and C. Also affected is the rate of solids circulation. The endothermic heat requirement is also significant as it directly affects the denominator in the definition of the efficiency.

CONCLUSIONS

The LASL bismuth sulfate cycle appears to be the most promising choice from a generic class of sulfate cycles that avoid the acid concentration step as well as the acid vaporization step in the conventional sulfuric acid based cycles under intensive development. For high efficiency, the overall cycle temperature should be high and the overall decomposition of the sulfate and subsequently sulfur trioxide should match the thermal delivery characteristics of an isothermal heat source such as fusion or solar energy as the decomposition reactions proceed isothermally. In this regard, these cycles would not adapt well to the heat delivery aspects of a high-temperature gas reactor (HTGR) as the latter resemble that of a counter-current heat exchanger (non-isothermal). Crucial issues to be resolved in the laboratory and in the field still remain; these include the demonstration of a low-voltage electrolyzer operating under production conditions, the recovery of latent heat from the solids drying operation, minimizing the amount of occluded water held by the solid sulfate precipitate, and the handling of large quantities of solids with attendant heat exchange in a high-temperature decomposer.

The promise of high efficiency for the utilization of high-temperature process heat to decompose water for hydrogen production remains as the major driving force in this activity.

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