United States Patent [19]

Birk

[11] **3,710,737**

[45] **Jan. 16, 1973**

[54] METHOD FOR PRODUCING HEAT

[75] Inventor: **James R. Birk,** Thousand Oaks, Calif.

[73] Assignee: **North American Rockwell Corporation**

[22] Filed: **Oct. 1, 1970**

[21] Appl. No.: **77,219**

[52] **U.S. Cl.** .....**110/1 J,** 110/7 R

[51] **Int. Cl.**.....**F23b 7/00**

[58] **Field of Search**.....110/1 P, 1 J, 7 R, 7 S, 8 R

[56] **References Cited**

UNITED STATES PATENTS

3,527,178 9/1970 Southwick.....110/8

3,642,583 2/1972 Greenberg et al.....110/8 X

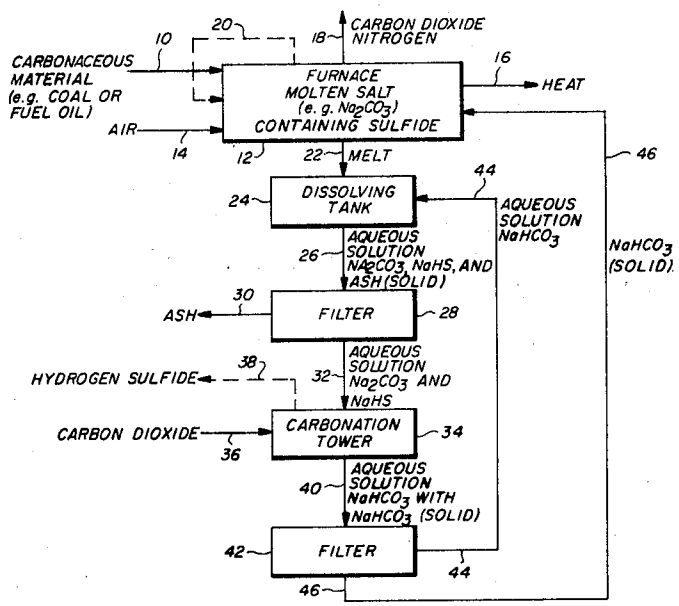
Primary Examiner—Kenneth W. Sprague

Attorney—L. Lee Humphries, Thomas S. MacDonald, Robert M. Davidson and Henry Kolin

[57] **ABSTRACT**

Heat is generated for external use by reacting a molten sulfide with a reactive form of oxygen such as air. The sulfate produced by this reaction is reduced to the sulfide form by contact with a carbonaceous material. A variety of carbonaceous materials may be used including common fuels and carbon-containing waste materials. Thus, the process can be used as a method of waste disposal as well as a method of generating heat.

18 Claims, 2 Drawing Figures



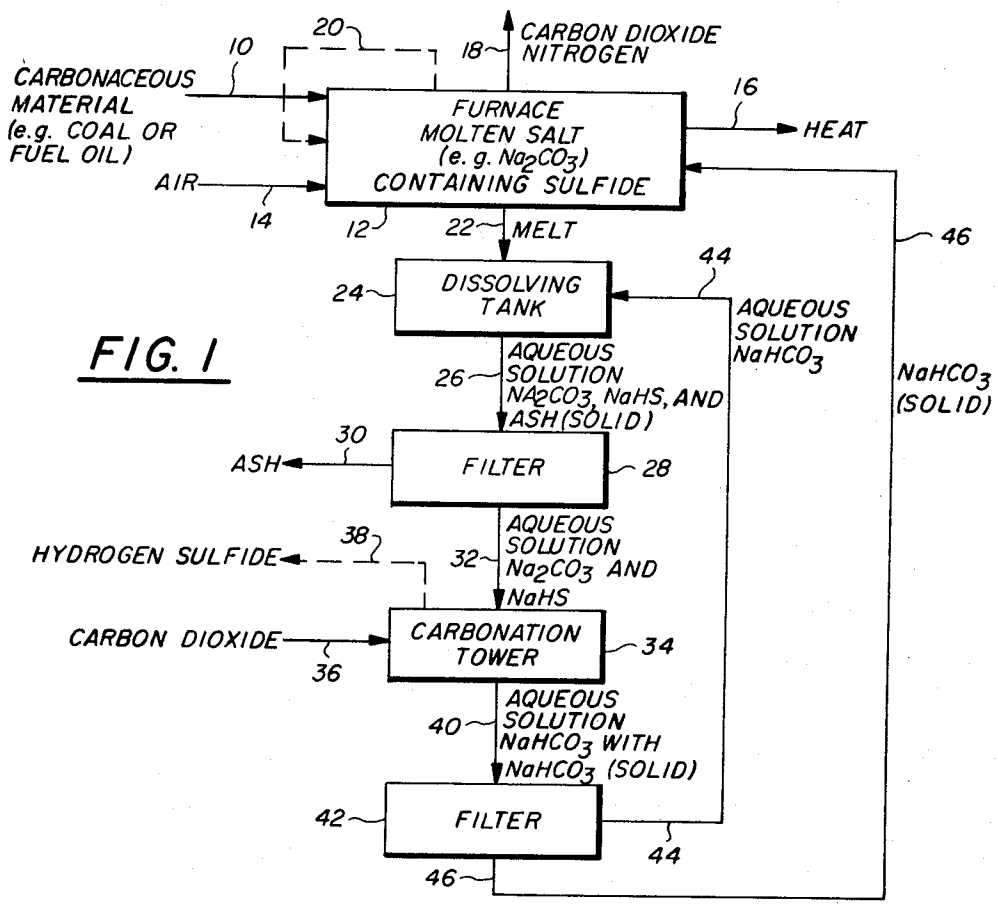


FIG. 1

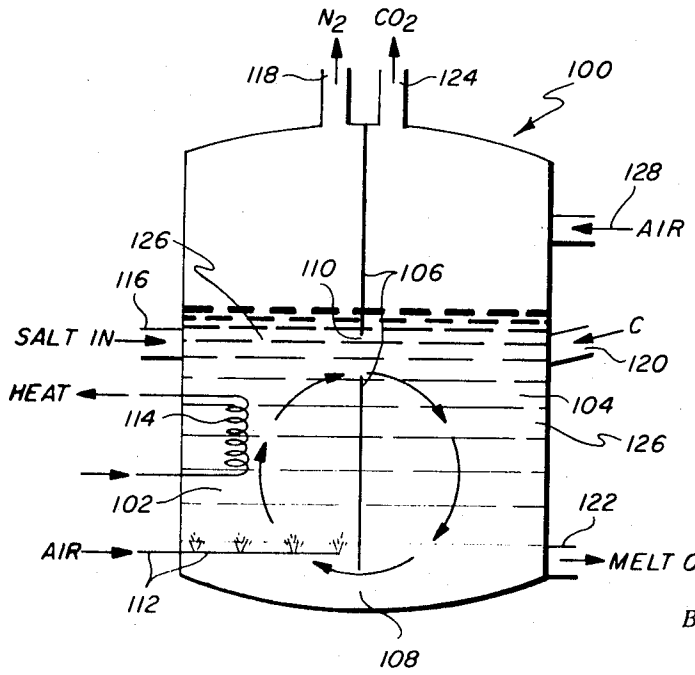


FIG. 2

INVENTOR.
JAMES R. BIRK

BY Robert M. Davidson

ATTORNEY

METHOD FOR PRODUCING HEAT

CROSS-REFERENCE TO RELATED APPLICATIONS

A method for pyrolyzing carbonaceous materials with attendant recovery of pyrolysis gases wherein the pyrolysis is accomplished in a molten salt mixture containing alkali metal sulfide and sulfate is described in copending U.S. Pat. application Ser. no. 77,255 by J. R. Birk and D. A. Huber entitled "Pyrolysis Method," filed concurrently herewith and commonly assigned with the present invention.

A method for converting hydrocarbons wherein the hydrocarbon feedstock is introduced into a molten salt mixture containing petroleum products is described in copending U.S. Pat. application Ser. No. 77,170 by L. A. Heredy and J. R. Birk entitled "Hydrocarbon Conversion Process," filed concurrently herewith and commonly assigned with the present application.

BACKGROUND OF THE INVENTION

A. Field of Invention

This invention relates to the field of heat generation. More particularly, it relates to the field of heat generation from a pair of cyclic reactions involving the consumption of carbonaceous materials. Still further, heat is generated for external use by reacting a molted sulfide with a reactive form of oxygen such as air. The sulfate produced by this reaction is reduced to the sulfide form by contact with a carbonaceous material. A variety of carbonaceous materials may be used including common fuels and carbon-containing waste materials. Thus, the process can be used as a method of waste disposal as well as a method of generating heat. The generation of heat from carbonaceous materials has been an important factor in the progress of civilization since man's discovery of fire. From that time forward, the prime source of man-made heat energy has been the combustion of carbonaceous materials such as wood, peat, coal, oil and gas with oxygen, usually in the form of air. The combustion process has taken place in piles, pits, beds, furnaces and engines for the purpose of heat per se or alternatively for the production of steam, mechanical energy or electrical energy. The conventional production of heat by combustion of carbonaceous materials is represented in part by the equation:

$$C + O_2 \rightarrow CO_2 + \text{heat}$$

It is often the case that other undesirable products such as CO, SO_2, SO_3, NO and NO_2 are formed during the combustion due to impurities in the fuel or the combustion technique employed. In order to prevent release of the atmosphere of many of the undesirable compounds, it is necessary to either restrict the use of fuels to only those having a very low amount of impurities; remove the impurities prior to combustion; or to remove the undesirable compounds formed by combustion from the gaseous effluent. The first alternative is wasteful of resources and the latter two have been found to be impractical in a great number of instances. Yet, if these problems can be overcome, the huge supply of carbonaceous fuel, particularly coal, would have more widespread use for the production of heat.

B. Description of the Prior Art

The conventional method of producing heat from carbonaceous materials as noted above, involves the direct oxidation usually with air to produce carbon dioxide. In this manner, millions of tons of carbonaceous fuels are combusted annually to produce heat for electric power generation and for industrial and residential heat. In addition, large amounts of low grade carbonaceous materials are combusted in incinerators as a method of waste disposal.

Various improvements have been made in the conventional combustion processes, particularly with respect to improving the efficiency of combustion of specific fuels. For example, the combustion of coal with air has been studied and improved over the past 100 years to the point where additional improvements in burner design or combustion conditions add only small increments to the efficiency of the process. The combustion of fuel oil and fuel gases have been similarly optimized.

The chemistry of the alkali metal sulfates has been extensively studied. Particularly well known is the ability of a variety of reducing agents to convert alkali metal sulfates to alkali metal sulfides. U. S. Pat. Nos. 461,674; 562,377; 700,132; 738,702; 1,397,497; 2,093,504; 2,106,952; 2,344,104; 2,414,042; 2,492,716; 2,690,958; 2,719,076; 2,837,403; 2,838,374; 2,903,336; 3,129,058 and 3,378,336 exemplify the reduction reaction. The oxidation of alkali metal sulfides is also a known reaction. The prior art, however, has never considered a combination of these reactions in a cyclic heat generation process. Rather the prior art when practicing one reaction scrupulously avoided the other.

The art of molten salt chemistry has made numerous recent advances. By virtue of their stability and wide liquid range, molten salts are being investigated for and used in a wide variety of applications. These include, for example, (1) reaction medium for production of aluminum, sodium, magnesium, and fluorine; (2) media for reprocessing spent reactor fuel elements; (3) electrolyte for fuel cells; (4) heat transfer agent and catalyst for hydrocracking petroleum residuals; (5) solvent for plating of refractory metals; (6) solvent for fluxing and descaling operations on metals; and (7) fuel solvent and heat transfer agent for nuclear reactors. U.S. Pat. No. 3,438,722 to L. A. Heredy is an example of such progress in the field of air pollution control. That patent described the absorption of sulfur oxides from flue gases in a molten alkali carbonate melt. However, the discovery embodied in that patent did not relate to the production of heat from carbonaceous materials. Carbonaceous materials have been treated in molten salt environments. Thus, in U. S. Pat. No. 3,252,773 to Solomon et al., a carbon containing solid material and steam are brought into contact with a melt comprising an alkali metal compound under conditions such that a hydrogen-rich gas is formed along with a resultant char. As an adjunct, heat may be supplied for the gasification reaction by combusting the resultant char with air. Hence, it is a requirement of this system that any heat generation occur as the result of the direct combustion of carbon by the reaction $C + O_2 \rightarrow CO_2$.

SUMMARY OF THE INVENTION

I have now discovered an improved method of generating heat. This method involves a two step process wherein the first step is the reaction of a molten sulfide with oxygen to produce a molten sulfate and useful heat. The second step involves the regeneration of the sulfide by contacting the molten sulfate with a carbonaceous material.

Accordingly, the objects of the present invention are:

- to provide an improved process for generating heat from carbonaceous materials;
- to provide a process for the generation of heat from carbonaceous materials having improved heat-exchange characteristics;
- to provide a process for heat generation from carbonaceous materials which obviates pollutant impurity removal prior to or after heat generation;
- to provide an improved process for the generation of heat from carbonaceous solids;
- to provide an improved process for the generation of heat from carbonaceous fluids;
- to provide an improved process for the treatment of carbonaceous waste materials; and
- to provide an improved process for the generation of heat from carbonaceous waste materials.

These and other objects and advantages of the invention will become more apparent upon consideration of the following detailed description of the preferred embodiments of the invention in which reference is made to the figures of the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic drawing showing a simplified flow-chart of a preferred embodiment of the present process.

FIG. 2 is a schematic drawing illustrating a preferred form of reactor for use in the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is broadly directed to the production of heat. A preferred form of the invention is directed to a cyclic dual reaction system occurring within a molten salt environment wherein heat is produced and oxygen is consumed in the first reaction and a carbonaceous substance is consumed in the second reaction. The two reactions can be carried out either simultaneously within a single unit or separately in two separate zones of a reaction vessel or in two separate reaction units.

The operation of the present invention is generally illustrated by the following reactions:

1. $M_2S + 2O_2 \rightarrow M_2SO_4$
2. $M_2SO_4 + 2C \rightarrow M_2S + 2CO_2\uparrow$

where M = Na, Li, K or mixtures thereof. Although carbon is shown as a reactant in reaction (2), any of the common fuels or decomposition products of common fuels can likewise take part in the reaction (e.g., $CH_4 + M_2SO_4 \rightarrow M_2S + CO_2 + 2H_2O$).

Reaction (1) is very exothermic whereas reaction (2) is endothermic. The composite of reactions (1) and (2) results in the liberation of the same amount of heat as the conventional oxidation of carbon to carbon dioxide. The transfer of heat is much easier than in conventional carbon combustion due to the higher heat transfer rates within the molten salts. In order to accomplish these reactions the temperature should be above 300°C for reaction (1) and above 600°C for reaction (2) and preferably between 800°C and 1,200°C for both reactions. These temperatures are far below the operating temperatures of most furnaces and boilers. These reactions can be carried out at any practical pressures; however, increased pressure decreases the volumetric throughput of gases through the molten salt.

In view of the cyclic nature of these reactions, it is not necessary that the melt contain only alkali metal sulfides or sulfates. Rather, it is preferred that the melt consist primarily of other salts which serve as a carrier or reaction medium. The salts used must be compatible with the alkali metal sulfides and sulfates at operating temperatures. A preferred class of salts is the alkali metal carbonates.

It is important that the melt contain a sulfur content of from about 1 to 25 and preferably from 2 to 10 weight percent based on sulfur. The amount should be sufficient to assure that reactions (1) and (2) above occur in preference to the reaction $C + O_2 \rightarrow CO_2$. In other words, substantially all of the carbon should be consumed by the mechanism of reaction (2).

Any reactive source of oxygen which is compatible with the melt and the reactants may be used. The most preferred form is air. In addition, if reactions (1) and (2) are simultaneously carried out while all the reactants are in intimate contact with each other, it is preferable that an excess of carbon be present so that under steady-state operating conditions, reaction (2) is favored and the sulfur present in the melt is in the sulfide form. Many forms of carbonaceous substances may be used as the reductant in this process. All common forms of carbonaceous fuels may be used including natural gas, coke, coal, fuel oils, petroleum residues, lignite, peat and wood. In addition, numerous waste materials not readily amenable to conventional combustion may be used in this process. For example, I contemplate the use of municipal wastes such as household trash and garbage, and sewage sludge; industrial wastes such as polyvinyl chloride, wood, rubber, plastics, used crankcase oil, or food processing wastes; and agricultural wastes including plant and animal waste materials.

In addition to a carbonaceous reductant and a reactive form of oxygen, it may sometimes be desirable to include a catalyst for the reduction reaction. Iron has been found to be a good catalyst for this reaction. Thus, an amount of iron ranging from about 0.5 to about 7 weight percent of the melt may be used. The iron may be added in the elemental form or in the form of compounds containing iron which are compatible with the other melt constituents such as iron sulfide or iron sulfate.

A preferred embodiment of this invention is illustrated in FIG. 1. For purposes of illustration, the composition of the melt will be represented in terms of sodium as the cation. As noted, however, the composition of the melt may include other metal ions. In FIG. 1, 10 represents a conventional carbonaceous fuel such as coal or fuel oil. The fuel supply 10 is fed to furnace or reactor 12. The particular design should provide for in-

timate contact between the carbonaceous feed and sulfate in the melt. A source of reactive oxygen **14** such as air is also supplied to furnace **12**. The air may be introduced in the bottom portion of the reactor zone so as to pass upwardly through the melt and thereby provide for an intimate mixing of the oxygen and sulfide. In the drawing, **16** illustrates the withdrawal of product heat. Normally heat withdrawal will occur by the use of indirect heat exchange. Thus, for example, if the heat is generated for the purpose of producing high pressure steam, it is contemplated that heat exchange coil may be placed directly into the melt thereby taking advantage of the very high heat-transfer coefficient of the melt.

Depending upon the nature of the carbonaceous fuel used, by-product gases, such as hydrocarbons, tars, oil, partially oxygenated organic compounds, carbon monoxide and mixtures thereof, may form which do not completely react with the sulfate ions before rising to the top of reactor **12**. In addition, carbon monoxide is a minor product of reactions (2) under most conditions. This gas, along with the unreacted by-product gases, may be combusted above the melt by using an optional air stream such as **128** shown in FIG. **2**, combusted in a separate furnace, recovered as a by-product, or recycled through the melt in reactor **12** as shown by stream **20** in the drawing. Carbon dioxide and steam from the reduction reaction and nitrogen from the air are vented from reactor **12** via line **18**.

The type of fuel used will also determine the nature of impurities that will accumulate within the melt. Ash and sulfur compounds are the major impurities. The rate of their accumulation is dependent upon the impurity content of the feed and its rate of use.

FIG. **2** illustrates a preferred form of reactor for use in the present invention. There, **100** represents a reactor vessel consisting of a sulfide oxidation zone **102** and a sulfate reduction zone **104** separated by a slotted partition **106**. Partition **106** is constructed with two major openings **108** and **110** which provide fluid communication between zones **102** and **104**. The sulfide oxidation zone **102** has associated therewith an air inlet and distributor system **112**, heat exchange means **114**, salt inlet **116** and gaseous outlet **118**. The sulfate reduction zone **104** has associated therewith a carbonaceous material inlet **120**, a melt outlet **122** and a gaseous outlet **124**.

In operation, the reactor is filled with melt **126** to a point higher than opening **10**. Air is supplied to oxidation zone **102** through distributor system **112**, causing sulfide salts to be oxidized to sulfate salts according to reaction (1). The introduction of air also causes an upwardly directed flow of melt in zone **102** bringing hot melt in contact with heat exchange member **114**. Heat exchange member **114** serves to withdraw a portion of the heat generated in the exothermic reaction. Nitrogen from the introduced air leaves the oxidation zone portion of the reactor via line **118**. Circular flow patterns developed in the melt cause oxidized salts to flow through opening **110** to reducing zone **104**. Here a source of carbonaceous material **120** is added to the melt thereby causing a reduction of the sulfate to the sulfide according to reaction (2). Carbon dioxide produced in this reaction exists the reactor vessel at **124**. Reduced melt from zone **104** is carried by established flow currents through opening **108** of partition **106** to zone **103**. A portion of melt **126** may be withdrawn at **122** for purposes of removing accumulated impurities. Pure salt is returned to the reactor vessel at **116**.

Alternatively, the partition **106** need not be present in reactor **100**. In this situation reactions (1) and (2) are carried out simultaneously. For this case it is preferable that an excess of carbon be present so that under steady state operating conditions reaction (2) is favored and the sulfur present in the melt is substantially all in the sulfide form. Under these conditions the oxygen reacts with sulfide in preference to reacting directly with carbon. In other words, substantially all the carbon will be consumed by the mechanism of reaction (2).

Returning now to FIG. **1**, it is seen that the impurity removal process is therein represented by four major stages. Melt **22** withdrawn from reactor **12** is fed to dissolving tank **24**. If desired, the melt may be cooled by heat exchange prior to entering tank **24**. Within the dissolving tank, the melt is brought into contact with an aqueous solution. In the preferred case shown, the melt is contacted with stream **44** which consists of a recycle aqueous solution of sodium bicarbonate. The bicarbonate of the recycle stream reacts with the sodium sulfide according to the reaction:

3. $NaHCO_3 + Na_2S \rightarrow Na_2CO_3 + NaHS$

to produce sodium carbonate and sodium bisulfide. The resulting mixture of soluble salts and insoluble ash is fed to a filter unit **28** or to any other similar conventional separatory apparatus where the ash is separated and removed via line **30**. Following removal of the insolubles, the aqueous solution is fed via line **32** to a carbonation tower **34** of conventional design wherein the solution is contacted with carbon dioxide at a temperature of from 50° to 120°C and a pressure of from about 10 to 150 psi. The result of carbonation is to convert the sodium bisulfide to sodium bicarbonate according to the following reaction:

4. $NaHS + CO_2 + H_2O \rightarrow NaHCO_3 + H_2S$

Hydrogen sulfide formed in this reaction is withdrawn via line **38** and may be supplied to a conventional plant for the production of sulfur or sulfuric acid.

A portion of the product bicarbonate is soluble and a portion is insoluble. The entire slurry is fed via line **40** to a filter unit **42** or conventional separatory unit where the soluble and insoluble portions are separated. The soluble portion is recycled via line **44** to dissolving tank **24** while the insoluble solid portion is returned via line **46** to reactor **12**.

By constantly withdrawing and treating a portion of the melt in this manner, the excessive build-up of sulfur and ash can be prevented.

As noted above, the amount of melt withdrawn for treatment and the amount of hydrogen sulfide obtained will depend upon the concentration of ash and sulfur in the carbonaceous feed. Generally, an amount of sulfur of from between about 1 and 25 percent and preferably 2 to 10 percent on a weight basis should be maintained in the furnace melt. The proper amount of sulfur content will depend upon the design of the reactor. The primary limitation is that sufficient sulfur be contained in the melt such that reactions (1) and (2) above are preferentially performed to the exclusion of the reac-

tion $C + O_2 \rightarrow CO_2$. If the reactor is divided into two zones wherein there is very little if any direct contact between the carbonaceous material and oxygen then the amount of sulfur required as a sulfide or sulfate is not as great. In the case where the design of the reactor causes intimate contact between the carbonaceous feed and the oxygen source higher reflux concentrations in the form of sulfide are required. Ash content should be kept below about 20 weight percent.

The production of heat using the process herein described possesses several important advantages over conventional methods. Heat generation and temperature can be precisely controlled by adjustment of the air flow rate. A second very important advantage of the present invention is the absence of pollutant emissions. Formation of nitrogen oxides is unfavorable at the low reaction temperatures experienced. Also, gaseous sulfur compounds are rapidly absorbed by the melt thereby preventing a major source of air pollution. Ash is also retained by the melt preventing particulate emission in the flue gas. The efficiency of the present process is very high in that the oxygen content of input air is completely and rapidly consumed. As a consequence very little heat is consumed in heating excess gases normally required in conventional combustion operations. Further, heat transfer rates within the liquid melt are substantially higher than in a conventional furnace or boiler where heat transfer must occur in a gaseous medium. In addition, it is expected that the power output per unit volume of a reactor according to the present invention is much higher than heretofore commercially obtained. Also, the present process is capable of producing heat from a wide variety of carbonaceous sources, and is operable over a very wide range of pressures.

The following examples are illustrative of the present invention.

EXAMPLE I

(Reduction of Sulfate by Coal)

The reduction of sulfate with coal was demonstrated in a test where a total of 17.1 grams of bituminous coal was added to a melt (100g Na_2CO_3, 100g K_2CO_3, and 100g Li_2CO_3) containing 60g of sodium sulfate at about 800°C. The test was done in a ceramic crucible. Samples were taken periodically and analyzed. The sulfate content was determined by a standard gravimetric technique. The results of the determination are given below in Table I.

TABLE I

Reduction of Sulfate with Coal

Time[a] (Min)	M_2SO_4	Percent Reduction
0	25.2	0.0
6	24.2	4.0
12	18.7	25.8
18	14.6	42.1
42.5	7.6	69.8
66.5	7.1	72.2
90	6.2	75.4

[a]Time after coal was initially added to the melt

These results demonstrated that 70 percent of the sulfate was reduced in a time of about 45 minutes.

EXAMPLE II

(Heat Generation)

In another similar test, 12.0g of coal were used to partially reduce 60g of sodium sulfate dissolved in 300g of an alkali carbonate melt. The temperature of the melt ranged from 840°–870°C. At the end of 15 minutes 44.7 percent of the sulfate was reduced to the sulfide; at the end of 25 minutes no further reduction of the sulfate had occurred. Therefore, the coal was assumed to have been completely expended during the reaction. The temperature of the system was allowed to stabilize. Air was then purged through the melt. At the instant the air purge was initiated, the temperature of the melt started to increase appreciably. It continued to increase until the air purge was stopped at which point the temperature of the melt began to decrease. For example, when air was purged through the melt at 2.1 l/min. the melt temperature rose from 891.5°C to 918°C in 3.0 minutes. Before and after the air purge, the melt was decreasing in temperature at a rate of about 6°C per minute.

EXAMPLE III

(Effect of Temperature and Iron on Reduction Rate)

Tests were carried out to determine the effect of iron and temperature on the reduction of sulfate with coke. For the control tests an alkali eutectic carbonate-sulfate melt containing 100.8g K_2CO_3, 100.8g Li_2CO_3, 37.0g Na_2CO_3, and 84.9g Na_2SO_4 (25 percent M_2SO_4) was reduced with 2.5 times stoichiometric coke (36 grams). To determine the effect of iron on the reduction rate the melt consisted initially of 100.8g K_2CO_3, 100.8g Li_2CO_3, 52.4g Na_2CO_3, 64.3g Na_2SO_4, and 40.3g $FeSO_4 \cdot 7HeO$ (25 percent M_2SO_4). Melt samples were taken periodically throughout each test and they were analyzed for sulfate, sulfide, and carbonate. The results of these tests are presented in Table 2.

TABLE II

Reductions with Coke

Conditions	Reduction Time (Hrs.)
600°C	91
700°C	2.9
700°C with Fe	1.9
800°C	0.50
800°C with Fe[a]	0.23

[a]Mechanical agitation, as opposed to agitation by means of a purge gas, was employed in this experiment.

The invention has been described herein with reference to preferred embodiments and specific examples. However, it will be apparent to those skilled in the art that many other modifications, adaptations and uses of this heat generation process are possible without departing from the spirit and scope of the invention as defined by the claims below.

I claim:

1. A method of generating heat and consuming carbonaceous materials comprising the steps of

A. contacting a melt containing alkali metal ions and sulfide ions ($S^=$) at a temperature of at least 300°C with a reactive form of oxygen thereby converting said sulfide ions to sulfate ions ($SO_4^=$),

B. contacting the sulfate ions formed in step (A) at a temperature of at least 600°C with a carbonaceous material such that said carbonaceous material is predominately consumed in the reaction,

$$SO_4^{=} + 2C \rightarrow S^{=} + 2CO_2, \text{ and}$$

C. returning the sulfide ions formed in step (B) to step (A).

2. The method of claim 1 wherein said carbonaceous material is selected from the group consisting of natural gas, coke, coal, fuel oil, petroleum residue, lignite, peat and wood.

3. The method of claim 1 wherein said carbonaceous material is a carbonaceous waste material.

4. The method of claim 1 wherein said melt has a sulfur content of from about 1 to about 25 weight percent.

5. The method of claim 1 wherein said melt has a sulfur content of from about 2 to about 10 weight percent.

6. The method of claim 1 wherein said melt contains carbonate ions.

7. The method of claim 1 wherein a portion of said melt is continuously treated to prevent a build-up in sulfur and ash content.

8. The method of claim 1 wherein said melt contains from about 0.5 to about 7 weight percent iron.

9. A method for generating heat and consuming carbonaceous materials comprising simultaneously contacting a melt containing alkali metal ions and sulfide ions ($S^{=}$) with a preselected amount of a reactive form of oxygen and with a sufficient amount of carbonaceous material such that the oxygen reacts with the sulfide according to the reaction:

$$S^{=} + 2O_2 \rightarrow SO_4^{=}$$

and the carbonaceous material is predominately consumed in the reaction:

$$SO_4^{=} + 2C \rightarrow S^{=} + 2CO_2,$$

and controlling said preselected amount of oxygen at less than that stoichiometrically required for oxidation of the carbonaceous material, which is present in excess in the melt, so that under steady-state operating conditions the sulfur present in the melt is maintained substantially all in sulfide form and substantially free of the sulfate form.

10. The method of claim 9 wherein said carbonaceous material is selected from the group consisting of natural gas, coke, coal, fuel oil, petroleum residues, lignite, peat and wood.

11. The method of claim 9 wherein said carbonaceous material is a waste material.

12. The method of claim 9 wherein said melt has a sulfur content of from about 1 to about 25 weight percent.

13. The method of claim 9 wherein said melt contains carbonate ions.

14. A method of producing heat and consuming carbonaceous materials comprising contacting a melt containing alkali metal ions and sulfide ions at a temperature of at least 300° C with a reactive form of oxygen to convert said sulfide to sulfate, and contacting said sulfate with a carbonaceous material to convert said sulfate to sulfide and to produce a by-product gas selected from the group consisting of hydrocarbons, tars, oils, partially oxygenated organic compounds, carbon monoxide and mixtures thereof.

15. The method of claim 14 wherein said by-product gas is combusted with air above said melt.

16. The method of claim 14 wherein a portion of said by-product gas is recycled through said melt.

17. The method of claim 14 wherein said melt contains from about 1 to about 25 weight percent sulfur.

18. The method of claim 17 wherein said melt contains carbonate ions.

* * * * *