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Applicant : **GENERAL ELECTRIC COMPANY**
1 River Road
Schenectady, NY 12345 (US)

Inventor : **Spiro, Clifford Lawrence**
1018 Mohawk Road
Schenectady, New York 12309 (US)
Inventor : **Peters, Herbert Clark**
37 Margaret Drive
Ballston Spa, New York 12020 (US)
Inventor : **Guggenheim, Thomas Link**
311 Heritage Drive
Mount Vernon, Indiana 47620 (US)
Inventor : **Allen, Timothy Mark**
1120 Char Lee Drive
Evansville, Indiana 47700 (US)

Representative : **Pratt, Richard Wilson et al**
London Patent Operation G.E. Technical
Services Co. Inc. Essex House 12/13 Essex
Street
London WC2R 3AA (GB)

Method and apparatus for destroying sodium-containing waste products.

Waste materials including organic and inorganic by-products and combined sodium in the amount of at least about 0.1%, and most often at least about 5%, by weight are destroyed by combustion at a temperature above about 700°C in a vessel lined with a refractory comprising at least about 85% by weight combined aluminum calculated as aluminum oxide. The refractory may be of sintered or fused-cast construction; if the former, it also comprises an aluminosilicate binder, preferably mullite, and contains at least about 6.5% combined silicon calculated as silicon dioxide. Such refractories have improved resistance to the corrosive effects of the sodium in the waste stream.

This invention relates to the destruction of waste materials, and more particularly to the combustion of waste streams which contain organic compounds and which are high in sodium.

5 A major cost element in chemical processes carried out on a commercial scale is the disposal of non-recyclable by-products and wastes. These may include organic and inorganic compounds, many of which are toxic or otherwise hazardous. Increased attention to environmental hazards has made it imperative to develop improved methods for disposing of such waste products. In particular, many of such products must be destroyed so that they do not pass into the environment and cause harm.

10 Among the industries demanding effective waste disposal is the plastics industry. Millions of pounds of plastic are produced per year, and almost every production process also creates large amounts of by-products and wastes.

A single example of a plastics production process which produces wastes is the process of making polyimides, and particularly polyetherimides. Many steps are involved, only a few of which need be described here to indicate the complexity of the waste materials which must be dealt with.

15 In a typical polyetherimide preparation method, an early step is the nitration of a phthalimide with nitric acid, which produces as wastes excess nitric acid and various nitro-substituted phthalic acid derivatives. The nitrophthalimide is slurried with water and the slurry is contacted with an organic solvent, whereupon the nitrophthalimide dissolves in the organic phase and leaves behind an aqueous waste containing traces of various compounds, organic and inorganic.

20 The nitrophthalimide in the organic solution undergoes a displacement reaction with the disodium salt of a dihydroxyaromatic compound such as 2,2-bis(4-hydroxyphenyl)propane, commonly designated bisphenol A, with the formation of a bisimide and sodium nitrite as a by-product. This displacement reaction ordinarily takes place in the presence of a phase transfer catalyst, traces of which may also be found in the waste stream. Numerous other by-products, as well as further quantities of those already mentioned, are removed by further extraction of the organic reactant solutions with aqueous sodium hydroxide. The bisimide subsequently undergoes further reactions to form the polyetherimide.

25 The complexity of the combined aqueous waste stream formed in this production process will be apparent from the above description. It contains large quantities of water, typically 60-80% and usually on the order of 70% by weight. About 15-30%, usually about 20%, is ordinarily nitrite ion (in the form of sodium nitrite) and about 5-10%, usually about 7-8%, various organic compounds, and the remainder includes sodium hydroxide. 30 The sodium ion content of the aqueous waste stream is substantial, often on the order of 5-15% and usually about 7-8% by weight. pH values may be in the range of about 2-12 but are usually on the alkaline side, typically about 10-12.

A typical waste disposal method for such by-products involves feeding the aqueous waste stream into a multi-stage destruction apparatus including oxidation/combustion and reduction stages. In such an apparatus, 35 organic compounds are combusted and nitrogen compounds converted to nitrogen oxides in one or more stages conducted in an oxygen-rich atmosphere. At least one other stage may be conducted in a reducing atmosphere created by the injection of natural gas, the effect of which is to convert nitrogen compounds to elemental nitrogen. All of these stages are carried out at very high temperature, typically on the order of 1000-1300°C.

40 The effect of sodium compounds under such conditions is profound and adverse. Even in concentrations as low as 0.1% by weight, sodium can corrode metal vessels so fast that such vessels, if unlined, are utterly useless as containers. A typical way to minimize such corrosion is to line the vessel with a refractory material. It has been found, however, that sodium is also profoundly destructive of most refractories. A majority of the sodium is converted to sodium oxide which subsequently reacts with carbon dioxide to form sodium carbonate. Any remaining sodium, however, reacts with the refractory material to produce a slag which spalls off the inside 45 surface of the chamber in varying quantities. The result is ultimate destruction of the refractory, exposing the bare metal to the action of the sodium and ultimately rupturing the vessel. As a side effect, large quantities of slag are produced and they complicate disposal of the treated waste stream. It has been estimated that as much as 90% of the deterioration of refractories in these environments is the result of corrosion by sodium compounds.

50 Various types of refractories have been evaluated for use in a process such as that described above. They are typically in the form of brick containing various proportions of combined aluminum, generally in combination with combined silicon and other combined metals and nonmetals. For the most part, however, such brick has been found to have a very short life when exposed to a waste stream high in sodium.

55 The present invention is based on the discovery of certain types of refractory materials high in aluminum which are particularly resistant to the corrosive effects of sodium compounds. Combustion chambers lined with these refractory materials are capable of undergoing hundreds of hours of contact at high temperatures without failing. Moreover, the slag produced when such refractories are used is small in volume and relatively easy to remove and dispose of.

Accordingly, the invention in one of its aspects is a method for destroying waste materials which comprises feeding a stream comprising waste products, including at least about 0.1% by weight combined sodium, to a treatment vessel, combusting said organic waste products at temperatures in the range of about 1000-1300°C and removing by-products including sodium compounds from said vessel,

the surface of said treatment vessel which contacts said waste products comprising a refractory material which comprises at least about 85% by weight combined aluminum calculated as aluminum oxide, and which, if of sintered construction, comprises alumina grains and an aluminosilicate binder and contains at least about 6.5% combined silicon calculated as silicon dioxide.

The drawing illustrates a typical combustion apparatus for wastes which may be employed in accordance with the invention.

The present invention is capable of employment to destroy a wide variety of organic and inorganic waste products. For the most part, it is advantageous in connection with waste streams containing organic chemicals and a relatively high concentration of sodium compounds, the latter being at least about 0.1% by weight and frequently at least about 5% by weight.

The vessel into which the waste stream is fed may be made of any non-porous material which is capable of withstanding the combustion temperatures of about 1000-1300°C attained during the process. Metals such as steel are typically used. It is necessary, however, that the interior surface which contacts the waste products be a suitable refractory material in order to prevent the rapid corrosion of metal which occurs upon contact with sodium compounds at the prevailing combustion temperatures.

Accordingly, the nature of the refractory lining of the vessel is a key feature of the invention. It should comprise at least about 85% and preferably at least about 90% combined aluminum by weight, calculated as aluminum oxide (alumina).

The fact that such materials effectively resist attack by sodium compounds is extremely unexpected, particularly in view of observations made by Caprio and Wolfe of Harbison-Walker Refractories in a paper entitled "Refractories for Hazardous Waste incineration-An Overview", in which it is observed that alkalies attack high-alumina refractories and the rate of attack is severe as the alumina content is increased to values on the order of 70%.

In sintered refractories, the presence and nature of a binder material are also critical. Said binder should comprise a major proportion of aluminosilicate, and should be present in sufficient amount to provide at least about 6.5% combined silicon, calculated as silicon dioxide (silica), in the refractory. Mullite is a particularly effective form of aluminosilicate for use as a binder.

If the refractory is of fused-cast construction, the alumina therein essentially serves as its own binder. In that case, the presence of a silicon-containing binder is not required, although it may be present in small proportions.

It is also generally important that the refractory be free from heavy metals, which may be environmentally harmful if present in the slag. For example, some refractories contain chromium which remains in the slag in the hexavalent state, known to be an environmental hazard. Such materials are unsatisfactory for the purposes of the invention.

The bulk density of the refractory used according to the present invention is generally at least about 2.9 g./cm.³. It is most often above 3.0 g./cm.³.

Various commercially available brick compositions have been identified which are particularly valuable for use according to the present invention. They include "Korundal XD" manufactured by Harbison-Walker Refractories, "GreenAl-90" manufactured by A.P. Green Industries, Inc., and "Monofrax Type M" and "Monofrax Type H" of The Carborundum Company. The essential properties of these materials are given in the following table.

	Korundal XD	GreenAl-90	Monofrax M	Monofrax H
Type *	S	S	F	F
Percent by weight:				
Al ₂ O ₃	90	90	95	93
SiO ₂	9	9	0.8	0.3
MgO	0.1	-	-	-
Fe ₂ O ₃	0.1	0.2	0.1	0.1
TiO ₂	0.1	0.1	-	-
CaO	0.1	-	0.2	0.1
Na ₂ O	-	0.2	4.0	6.0
P ₂ O ₅	-	1.5	-	-

*S—sintered; F—fused—cast.

Several things are noticeable in the above table. In the first place, the proportions of sodium in the fused-cast bricks are substantially higher than those in the sintered bricks. No position is taken in connection with the present invention on whether it is necessary to minimize the proportion of sodium in sintered bricks.

In the second place, the silicon proportion is substantially higher in sintered than in fused-cast brick. The reason for this is essentially the one described hereinabove; no binder, which is the aluminosilicate-containing and therefore the predominant silicon-containing constituent, is necessary in the fused-cast brick, but one is necessary in the sintered brick.

In the third place, "GreenAl-90" differs from the other bricks in containing 1.5% phosphorus as phosphorus pentoxide. In actual plant installations, "GreenAl-90" has been found slightly superior to "Korundal XD" in wear characteristics. Accordingly, in a preferred embodiment of the invention the refractory also contains at least about 1% combined phosphorus as P₂O₅.

The slag produced in the method of this invention may vary in nature from a uniformly granular material to one which is thick and flowable near the refractory surface and more granular at a distance from said surface. The formation of a thick, flowable slag is frequently advantageous in that less shearing of the pebbles from the refractory surface may occur than with a granular slag.

The organic constituents of the waste stream are combusted in the aforementioned vessel, at temperatures above about 700°C and most often in the range of about 1000-1300°C. The precise nature of the combustion step is not critical for the purposes of this invention. Most often, however, it comprises at least one oxidizing and at least one reducing step, conducted under fuel-lean and fuel-rich conditions, respectively. The fuel is normally natural gas and is employed in admixture with an oxygen-containing gas, typically air.

A typical combustion operation according to the invention utilizes the apparatus shown in the drawing. The waste stream is charged at 2 to the top zone 4 of a three-zone combustion stack 1, where it is contacted with air and natural gas entering at 6 and 8, respectively. The stream then passes downward via passage 10 into second zone 12, and finally through passage 16 into third zone 18.

Additional natural gas and air are introduced via nozzles 14 and 20, producing fuel-rich or fuel-lean zones as desired to result in reduction of the nitrogen oxides to elemental nitrogen or oxidation of nitrogen compounds to nitrogen oxides, respectively.

From zone 18, the vapors of the waste stream are passed through downcomer 22 where they are quenched and removed by contact with water introduced through water jet 24. Volatile components are removed via at least one gas conduit, with two being shown at 26 and 28, and may be passed to scrubbers for further treatment. Liquid components, predominantly water, are removed from quench tank 30 through liquid conduit 32.

In terms of construction, combustion stack 1 includes an external metal shell 34, typically of steel, and an inner refractory lining 36, typically of brick as previously described. The thickness of lining 36 will vary with the conditions but is generally on the order of 15-30 cm., with about 20-25 cm. often being preferred.

In the course of the waste treatment process in stack 1, attack by sodium compounds on lining 36 often causes spalling of said lining in the form of pieces of various sizes, ranging from small particles to large chunks. Most of the larger pieces are caught by grate 38, with smaller particles passing through said grate and being caught in funnel 40.

Prior to the present invention, some pieces dislodged by spalling were so large that they could penetrate the wall of downcomer 22 and fall elsewhere in quench tank 30. They were known on occasion to be so hot that they caused vaporization of the liquid in the quench tank, occasionally resulting in rupture of safety pres-

sure disks in the system. The present invention has materially reduced the amount of spalling and alleviated this problem.

Another aspect of the invention is apparatus, of the type illustrated in the drawing, for destruction of waste materials. Said apparatus comprises a plurality of intercommunicating vertically disposed combustion stacks, means for feeding waste and fuel materials to the uppermost of said stacks, and a downcomer from the lowermost of said stacks. Each of said stacks, and each passage connecting them, has its inner surface lined with the above-described refractory. Said apparatus optionally further comprises fuel-lean and fuel-rich zones and means for supplying oxygen-containing gas and fuel, respectively, to said zones, as described hereinabove.

Various advantageous results of the present invention will be apparent to those skilled in the art. For example, the treatment system can be operated for substantially longer periods without deterioration of the interior of the treatment vessel. Further, the essential elimination of spalled refractory causes a substantial decrease or even elimination of the operational and cost burdens of conveying such material to a landfill.

The overall result, with particular reference to the substitution of a 23-cm. thickness of "GreenAl-90" for a similar thickness of a refractory substantially lower in aluminum and higher in silicon, has been to decrease down time of the unit and increase waste stream capacity by 90% and 36%, respectively. A waste destruction unit according to the invention can operate without down time for periods of at least 128 days.

Claims

1. A method for destroying waste materials which comprises feeding a stream comprising waste products, including at least about 0.1% by weight combined sodium, to a treatment vessel, combusting said organic waste products at temperatures in the range of about 1000-1300°C and removing by-products including sodium compounds from said vessel,
the surface of said treatment vessel which contacts said waste products comprising a refractory material which comprises at least about 85% by weight combined aluminum calculated as aluminum oxide, and which, if of sintered construction, comprises alumina grains and an aluminosilicate binder and contains at least about 6.5% combined silicon calculated as silicon dioxide.
2. A method according to claim 1 wherein the refractory is free from heavy metals.
3. A method according to Claim 1 or Claim 2 wherein the waste products include nitrite ion in the amount of about 15-30% by weight.
4. A method according to any preceding claim wherein the refractory material comprises at least about 90% aluminum oxide.
5. A method according to any preceding claim wherein the concentration of combined sodium in the waste products is at least about 5% by weight.
6. A method according to any preceding claim wherein the bulk density of the refractory is at least about 2.9 g./cm.³.
7. A method according to any one of Claims 1 to 6 wherein the refractory is of fused-cast construction.
8. A method according to any one of Claims 1 to 6 wherein the refractory is of sintered construction.
9. A method according to claim 8 wherein the aluminosilicate in the binder is mullite.
10. A method according to claim 8 wherein the binder contains at least about 1% combined phosphorus as P₂O₅.
11. A method according to any preceding claim wherein the combustion operation comprises at least one oxidizing and at least one reducing step, conducted under fuel-lean and fuel-rich conditions, respectively.
12. Apparatus for destroying waste materials, comprising a plurality of intercommunicating vertically disposed combustion stacks, means for feeding waste and fuel materials and an oxygen-containing gas to the uppermost of said stacks, and a downcomer from the lowermost of said stacks; each of said stacks, and

each passage connecting them, having its inner surface lined with a refractory material which comprises at least about 85% by weight combined aluminum calculated as aluminum oxide, and which, if of sintered construction, comprises alumina grains and an aluminosilicate binder and contains at least about 6.5% combined silicon calculated as silicon dioxide.

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13. Apparatus according to claim 12 wherein the refractory is free from heavy metals.

14. Apparatus according to Claim 12 or Claim 13 wherein the refractory material comprises at least about 90% aluminum oxide.

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15. Apparatus according to any one of Claims 12 to 14 wherein the bulk density of the refractory is at least about 2.9 g./cm.³.

16. Apparatus according to any one of Claims 12 to 15 wherein the refractory is of fused-cast construction.

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17. Apparatus according to any one of Claims 12 to 15 wherein the refractory is of sintered construction.

18. Apparatus according to claim 17 wherein the aluminosilicate in the binder is mullite.

19. Apparatus according to claim 17 wherein the binder contains at least about 1% phosphorus as P₂O₅.

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20. Apparatus according to any one of Claims 12 to 19 which additionally comprises fuel-lean and fuel-rich zones and means for supplying oxygen-containing gas and fuel, respectively, to said zones.

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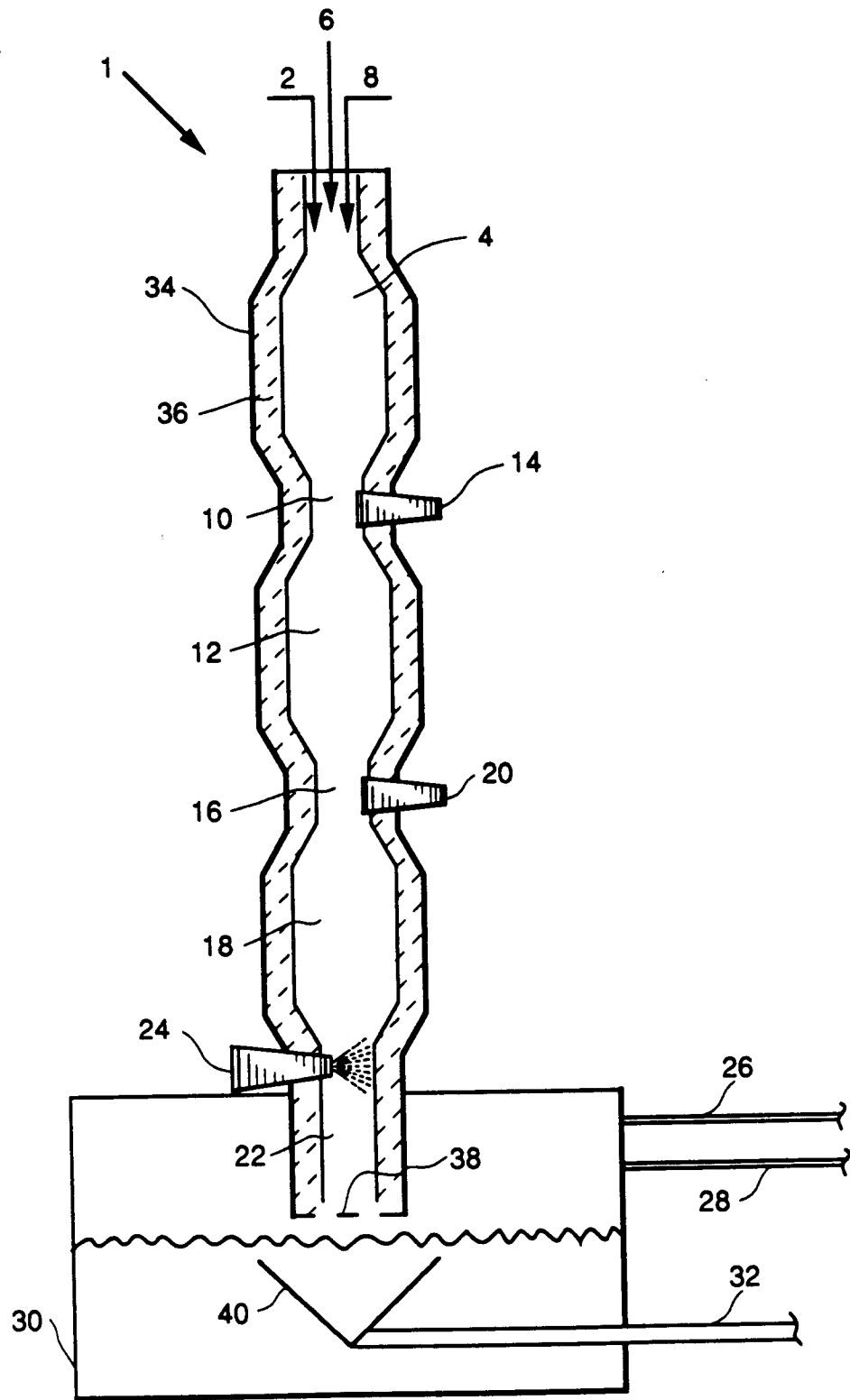
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 5848

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-4 237 103 (PRIBLE) * column 3, line 63 - column 4, line 64; figure 1 *	1,2,4,5	F23G5/48 F23M5/00 F23G7/00
Y	---	3,6,7, 11-16,20	
Y	DE-A-30 04 186 (NITTETU) * the whole document *	11-14,20	
Y	FR-A-2 219 910 (SPEICHIM) * page 3, line 18 - line 26; claim 1; figure 1; example *	3	
Y	POWER vol. 136, no. 1, January 1992, NEW YORK US pages 54 - 57 CROWLEY 'Know causes of, solutions to CFB-boiler refractory problems' * the whole document *	6,15	
A	---	9,10,18, 19	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
Y	GB-A-2 020 403 (HEENAN ENV. SYSTEMS) * abstract * * page 2, line 12 - line 20; figure 1 *	7,16	F23G F23M
A	US-A-3 712 796 (SANSOM) * column 2, line 44 - line 54 * * column 3, line 30 - line 41 * * column 4, line 34 - line 41; figures 1,2 *	1,12	
A,P	DE-A-41 28 963 (FEUERFEST) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 November 1993	Examiner COLI, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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