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Cowley

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[54] **CHLORINE DIOXIDE GENERATOR**

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[73] Assignee: **ERCO Industries Limited**, Islington, Canada

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Related U.S. Application Data

[62] Division of Ser. No. 964,681, Nov. 29, 1978, Pat. No. 4,203,961.

[51] **Int. Cl.**[3] **B01J 8/00**; B01D 45/16; B01J 19/02; C01B 11/02

[52] **U.S. Cl.** **422/187**; 422/189; 422/235; 422/240

[58] **Field of Search** ..... 55/92, 204, 237, 238, 55/459 B; 422/129, 187, 228, 234, 189, 235, 240, 245; 423/477, 478, 659

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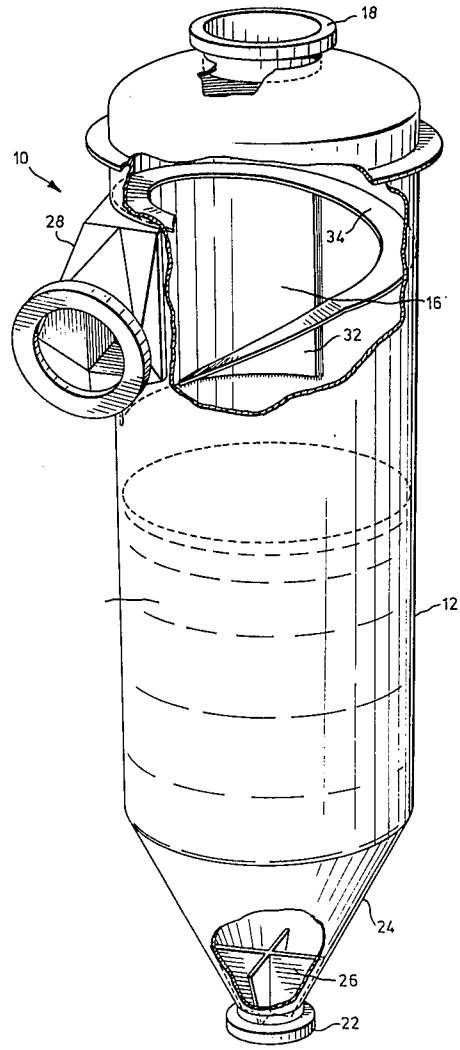
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[57] **ABSTRACT**

The entrainment of reaction medium in the vapor phase is decreased in a chlorine dioxide generator producing a gaseous mixture of chlorine dioxide, chlorine and steam from a boiling reaction medium and wherein generator liquor is recycled with make up chemicals by providing a tangential entry of recycled liquor to the generator in the vapor space above the liquid level in the generator and a helically-arranged baffle projecting inwardly from the generator wall at least in the height of the generator corresponding to the tangential entry opening into the vapor space. The baffle is arranged to be above the trajectory of the recycled liquor as it enters the generator. Decreased liquor entrainment enables the generator diameter to be decreased, with consequentially decreased capital costs.

12 Claims, 4 Drawing Figures



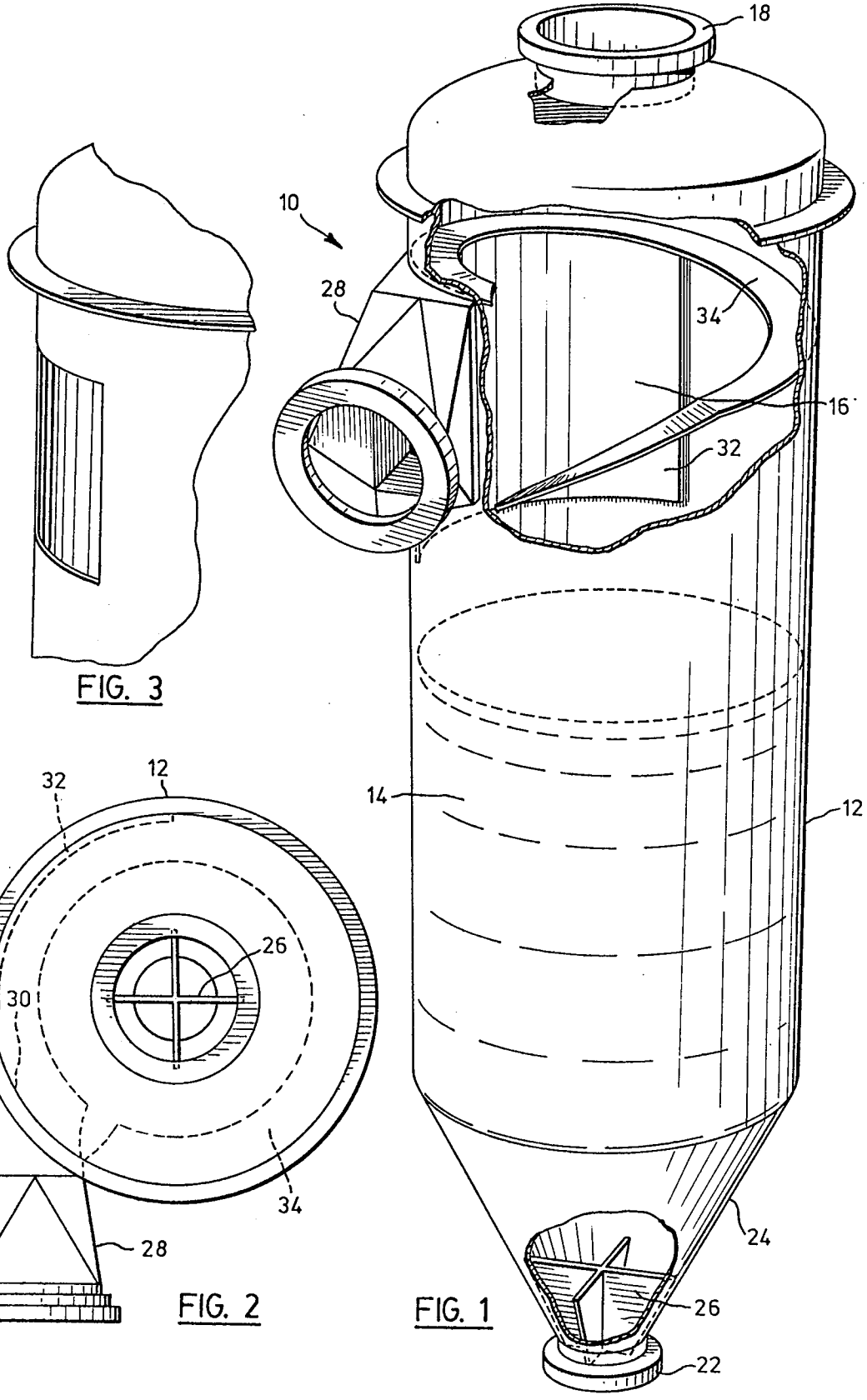


FIG. 1

FIG. 3

FIG. 2

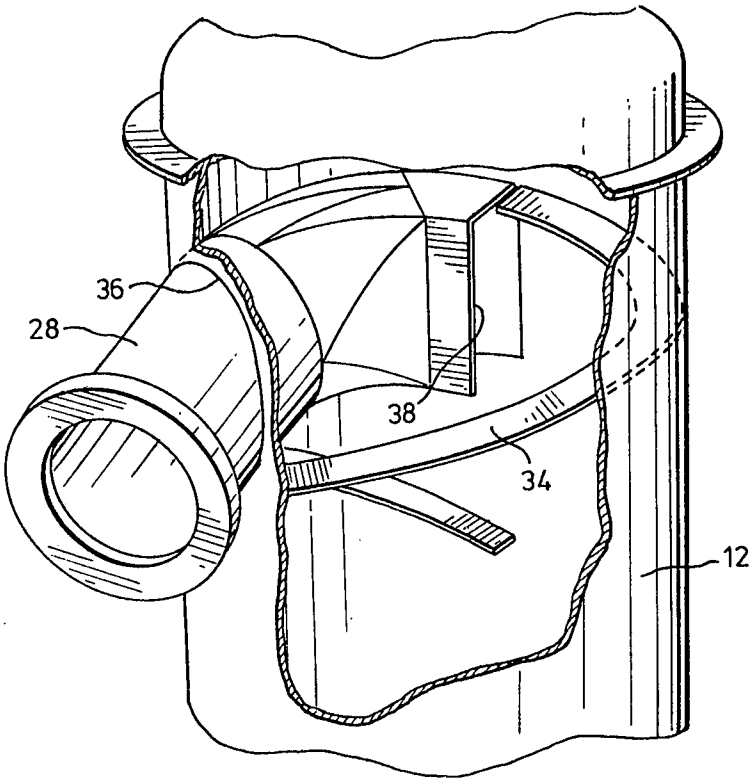


FIG. 4

CHLORINE DIOXIDE GENERATOR

This is a division of application Ser. No. 964,681, filed Nov. 29, 1978, now U.S. Pat. No. 4,203,961, issued May 20, 1980.

FIELD OF INVENTION

The present invention relates to a novel chlorine dioxide generator and to the production of chlorine dioxide using such generator.

BACKGROUND TO THE INVENTION

Chlorine dioxide is utilized in a variety of bleaching operations, particularly in the bleaching of cellulosic fibrous material, such as, wood pulp. In U.S. Pat. Nos. 3,895,100 and 3,975,506 assigned to the assignee of this application, the disclosures of which are incorporated herein by reference, there is disclosed a chlorine dioxide generating process and equipment therefor wherein chlorine dioxide is formed in a generally cylindrical upright reaction vessel by reduction of an alkali metal chlorate, usually sodium chlorate, with chloride ions in an aqueous acid reaction medium, in accordance with the equation:

$$ClO_3^- + Cl^- + 2H^+ \rightarrow ClO_2 + \tfrac{1}{2}Cl_2 + H_2O$$

The reaction medium in the generator is maintained at its boiling point, generally about 25° to about 90° C., under a subatmospheric pressure, generally about 20 to about 400 mm Hg, to cause the deposition of a by-product salt from the reaction medium in the generation vessel once saturation has been achieved after start-up and to remove the chlorine dioxide and chlorine in gaseous admixture with steam.

The by-product salt which is precipitated depends on the acid used in the reaction medium, the by-product being a sodium sulphate when sulphuric acid is used and sodium chloride and/or hydrogen chloride provide the chloride ion reducing agent, and the by-product being sodium chloride when hydrochloric acid is used and also provides the reducing agent.

When sulphuric acid is used, the sodium sulphate may be in an acidic or neutral form depending on the total acid normality of the generator, with a neutral salt generally being obtained at total acid normalities of about 2 to about 5 normal and acid salts being obtained at higher values usually up to about 12 normal.

When the total acid normality of a sulphuric acid based system is such as to produce neutral sodium sulphate, it is preferred to use a reaction temperature above about 30° C. in order to obtain the anhydrous salt.

When hydrochloric acid is used, the actual hydrogen ion concentration in the reaction medium is maintained in the range of about 0.05 to about 0.3 normal. The term "actual hydrogen ion concentration", as used herein, is the value determined by a pH meter calibrated on an 0.1 normal solution of hydrochloric acid on the assumption that such a solution is 100% dissociated at this concentration.

As described in the above-mentioned patents, the solid by-product is removed as a slurry in reaction medium from the generator vessel, sodium chlorate solution is mixed therewith, the mixture is recycled through a reboiler wherein the mixture is heated to the reaction temperature and forwarded to the reaction vessel after the addition of acid to the heated mixture. A portion of the slurry is withdrawn prior to the reboiler for crystal separation.

The heated mixture from the reboiler is passed through a venturi-like pipe which exerts sufficient back pressure on the mixture in the reboiler to prevent boiling therein, acid in concentrated form is introduced to the collar of the venturi and the resultant reaction mixture is allowed to expand at low acceleration to permit boiling and gaseous product formation to occur evenly and gradually and thereby avoid bumping and vibration, so that a fluid mixture of solid phase, liquid phase and gaseous phase enters the generator generally radially of the generator above the liquid level therein through a curved pipe joining the downstream end of the venturi-like pipe and the generation vessel inlet.

While this prior art procedure represents an excellent commercially-viable chlorine dioxide generating system having many advantages over prior art arrangements, as described in the above-mentioned patents, it has been found that entrainment of liquid and solid phases in the gaseous phase occurs, necessitating a considerable vapor space in the generator to achieve separation of the entrained material by the action of gravitational forces, otherwise the entrained material passes out of the generator with the removed gases, presenting problems in later-processing of the gases and is considered undesirable.

One prior art suggestion for overcoming the entrainment problem without the use of excessive vapor space is to use an internal demister, as described, for example, in U.S. Pat. No. 4,079,123, but such demisters, consisting usually of wire mesh through which the vapor phase passes and on which the liquid droplets impinge, are prone to clogging especially since the solid phase is also present, and hence must be cleaned frequently if chlorine dioxide production is to be sustained.

SUMMARY OF INVENTION

In accordance with the present invention, modifications to the generation system described in our U.S. Pat. No. 3,895,100 are effected in order to decrease entrainment of liquid and solid in the vapor phase and thereby permit a decrease in the vapor space volume without the need to use mesh or other type demisters.

The modifications involve provision of tangential entry for recycled liquor to the vapor space and provision of substantially helically-arranged baffle means projecting from the internal wall of the generator and extending substantially through 360° of turn in the vertical height of the tangential entry opening in location above the theoretical trajectory of liquor tangentially entering the generator and passing around the internal wall.

The tangential entry of the recycled mixture and the provision of the baffle means combine to decrease entrainment of liquid and solid phases in the gaseous phase, so that a smaller diameter vessel of lesser vapor space volume may be used to achieve gravitational separation of the material which is entrained.

Provision of a smaller diameter generator results in less material of construction being necessary for the generator, which usually is constructed of titanium owing to its high corrosion and wear resistance and excellent constructional qualities.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a perspective view with parts cut away of a chlorine dioxide generator constructed in accordance with one preferred embodiment of the invention; and

FIG. 2 is a view from below of the generator of FIG. 1,

FIG. 3 is a detail view of part of the generator of FIG. 1 with the entry pipe removed; and

FIG. 4 is a perspective view, with parts cut away, of part of a chlorine dioxide generator constructed in accordance with a second embodiment of the invention.

DESCRIPTION OF PREFERRED EMBODIMENT

Referring first to FIGS. 1 to 3 of the drawings, a chlorine dioxide generator **10** constructed in accordance with a preferred embodiment of the invention and representing the current best mode of the invention known to the inventor, comprises a generally cylindrical upright vessel **12** fabricated of any convenient corrosion-and wear-resistant material, preferably titanium.

The generator vessel **12** contains liquid reaction medium **14** which produces a gaseous mixture of chlorine dioxide, chlorine and steam which is removed from the vapor space **16** above the liquid level through a gaseous outlet **18** located in a top closure **20**.

The reaction medium **14** is maintained at its boiling point under a subatmospheric pressure applied to the vapor space **16** through the gaseous outlet **18**. In continuous operation, a solid by-product salt precipitates from the liquid reaction medium **14** and is removed through a solid outlet **22** located at the lower end of the vessel **12** in communication with a conical bottom closure element **24** as a slurry with reaction medium. The slurry then is processed to remove part of the solid phase and a recycle heated reaction mixture is formed, as described in detail in U.S. Pat. No. 3,895,100, referred to above.

A vortex breaker element **26**, consisting of perpendicularly arranged baffles, is located in the bottom closure **24** adjacent the slurry outlet **22** to break up rotational movement of the reaction medium **14** adjacent the slurry outlet **22**.

The heated reaction mixture recycle pipe illustrated in U.S. Pat. No. 3,895,100 communicates with a horizontally-directed inlet pipe **28** which increases in cross-sectional area in the direction of flow of the reaction mixture and terminates in a rectangular opening **30** in the side wall of the generator vessel **12** above the level of the reaction medium **14**. The inlet pipe **28** extends generally tangentially to the vessel wall so that recycled heated reaction mixture enters the vapor space **16** generally tangentially to the internal wall of the generator vessel **12**.

The recycled heated reaction mixture contains crystalline by-product salt which is abrasive in character. Although titanium is a highly wear-resistant material, it is preferred to construct the vessel **12** with a titanium liner **32** at least in the initial region of movement of the recycled heated reaction mixture between its entry to the vessel **12** and the reaction medium **14**. In the event of excessive wear, the liner **32** may be replaced.

Extending horizontally inwardly from the internal wall of the vessel **12** is a baffle **34**. The baffle **34** extends in generally helical manner from a location just above the inlet opening **30** through 360° of turn to terminate just below the level of the inlet opening **30**. The baffle **34** may extend further, if desired, into the reaction medium **14**.

The location of the baffle **34** is important to this invention and should approximate but be located above the intended trajectory of the recycled reaction mixture along the internal wall of the vessel **12** to the reaction medium **14**.

The location of the baffle **34** above the intended trajectory prevents impingement of the mixture thereon which may impair liquid separation and cause liquid to climb up the internal wall of the generator vessel **12**.

Any liquor which does rise up the internal wall of the generator vessel **12** above the baffle **34** is prevented from entering the outlet pipe **18** by the downward projection of the cylindrical outlet pipe inside the generator vessel **12**, as illustrated.

The baffle **34** prevents the gaseous phase in the recycled reaction mixture entering through opening **30**, which is a fluid mixture of liquid phase, solid phase and gaseous phase as described in U.S. Pat. No. 3,895,100, from proceeding upwardly in the vapor space **16**, taking with it entrained liquid and solid phases. Instead, the baffle **34** forces the gaseous phase initially to follow the trajectory of the liquid and solid phases and to move effectively radially of the internal wall of the vessel **12** before moving upwardly in the vapor space **16** when it clears the radially inner edge of the baffle **34**.

This gaseous phase motion causes separation of liquid and solid phases which tend to remain in the same trajectory and hence entrainment of these materials in the gaseous phase is decreased, permitting the cross-sectional area of the generator vessel **12** to be decreased, as compared with the radial-entry and no-baffle arrangement illustrated in U.S. Pat. No. 3,895,100. For example, for a given reaction vessel of a given chlorine dioxide production capacity and operating under the same conditions and flow rates, the overall generator vessel **12** cross-sectional area may be decreased by about 40% through the use of this invention.

For ease of fabrication of the baffle **34**, it is usually constructed, as illustrated, of a plurality of segments which are joined to form a continuous baffle, each segment typically extending for 90° of turn or a multiple thereof with its slope being rectilinear from end to end and approximating the average of the trajectory of the liquid passing around the internal wall in the particular curvilinear region of location of the baffle segment.

Alternatively, the baffle **34** may be provided as a continuous baffle which is continuously shaped along its length to approximate at any given location the trajectory of the liquid passing around the internal wall of the generator vessel **12**.

The required location and slope of the baffle **34** depends on a number of factors, including the velocity of the fluid entering the port **30** and the internal diameter of the generator vessel **12**, and can be readily calculated using conventional engineering principles.

The transverse dimension, or width, of the baffle **34** may vary widely and is generally related to the width of the rectangular inlet port **30**. Preferably, the width of the baffle **34** is about 30 to about 60 percent of the width of the rectangular inlet port **30**, and most preferably about one-half of the width, since the most efficient separation of entrained material occurs at this dimension.

The rectangular inlet port **30** is dimensioned in relationship to the internal diameter of the generator vessel **12**, so that the width is less than, and preferably approx-

mately equal to, about 25 percent of the internal diameter of the vessel **12**, since liquid separation from the gaseous phase is generally less satisfactory at higher values.

The inlet port **30** is illustrated as rectangular in shape, but any other desired shape may be used, for example, circular or oval.

The tangential entry of recycled reaction mixture to the generator vessel **12** under the influence of energy imparted thereto by expanding steam in the recycle pipe causes the reaction medium **14** to rotate in the generator vessel and to acquire the steam-imparted energy. In place of breaking this motion at the outlet port **22** using the vortex breaker **26** as illustrated, a tangential outlet may be provided adjacent a suitably-designed bottom closure and the motion energy of the exiting reaction medium may be used to replace part of the pumping energy required for recirculation, so that the overall energy requirements of the system are decreased.

DESCRIPTION OF ALTERNATIVE EMBODIMENT

Referring now to FIG. **4**, wherein there is disclosed an alternative recycled heated reaction mixture entry arrangement, the same reference numerals are used to identify the same parts as are described above in connection with the embodiment of FIGS. **1** to **3**.

In the embodiment of FIG. **4**, instead of the inlet pipe **28** terminating at a rectangular or other shaped opening **30** in the wall of the vessel **12** to achieve tangential entry, the pipe **28** passes through an opening **36** in the wall of the vessel **12** in sealing relationship therewith and then follows the internal wall of the vessel **12** to terminate in a rectangularly-shaped opening **38** to establish the tangential entry. The baffle **34** commences immediately at the termination of the inlet pipe **28**.

The dimensional relationships described above with respect to FIGS. **1** to **3** between the baffle **34** and the rectangular opening **30** apply in connection with the embodiment of FIG. **4** as between the baffle **34** and the rectangular opening **38**.

While the rectangular opening **38** and the passageway leading thereto in the increasing cross-sectional area of the inlet pipe **28** may be enclosed on four sides, it is preferred, as illustrated, to omit the bottom wall.

SUMMARY OF DISCLOSURE

The present invention, therefore, provides a chlorine dioxide generator having advantages over other prior art equipment wherein a fluid recycle stream consisting of a recycle mixture of gaseous phase, solid phase and liquid phase enters the vapor space of the generator. Modifications are possible within the scope of the invention.

What I claim is:

1. A chlorine dioxide generator comprising

a generally cylindrical body having upper and lower end closures, gaseous outlet means located in or adjacent to said upper end closure and slurry outlet means located in or adjacent to said lower end closure,

inlet means arranged tangentially to said cylindrical body terminating at its downstream end in communication with the interior of said body above the intended liquid level therein and below said gaseous outlet means for projection of reaction mixture into said body generally tangentially thereto, and

baffle means projecting substantially horizontally inwardly from the internal wall of said cylindrical body and extending in generally helical manner through 360° of turn from the upper extremity of the termination of said inlet means to the lower extremity thereof and arranged to be located above and follow substantially the flow path of said reaction mixture entering said generator.

2. The generator of claim **1** wherein said inlet means terminates at its downstream end in a side wall opening of said body.

3. The generator of claim **1** wherein said inlet means extends through the side wall of said body and terminates at its downstream end in the interior of said body.

4. The generator of claim **1** wherein said inlet means increases in cross-sectional area between the upstream and downstream ends thereof and terminates at its downstream end in a generally rectangularly-shaped opening.

5. The generator of claim **4** wherein said baffle means has a transverse dimension which is approximately one half of the width of said generally rectangularly-shaped opening.

6. The generator of claim **4** or **5** wherein said rectangularly-shaped opening has a width which is less than or equal to about 25% of the diameter of said cylindrical body.

7. The generator of claim **6** wherein said rectangularly-shaped opening width is approximately 25% of the cylindrical body diameter.

8. The generator of claim **1** or **4** wherein said baffle means comprises a plurality of individual baffle segments joined to form a continuous baffle.

9. The generator of claim **8** wherein each said baffle segment has a rectilinear slope from end to end which approximates the average intended trajectory of the reaction mixture entering the generator.

10. The generator of claim **1** or **4** including vortex breaker means located adjacent said slurry outlet means.

11. The generator of claim **1** or **4** including sleeve means located on the internal wall of the cylindrical body in the region of said baffle means and extending for at least part of the arc of the internal wall from the downstream end of said inlet means in the direction of intended motion of said reaction mixture.

12. The generator of claim **1** or **4** constructed of titanium.

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