



(86) Date de dépôt PCT/PCT Filing Date: 2007/02/23
(87) Date publication PCT/PCT Publication Date: 2007/09/07
(45) Date de délivrance/Issue Date: 2012/01/03
(85) Entrée phase nationale/National Entry: 2008/08/18
(86) N° demande PCT/PCT Application No.: US 2007/004894
(87) N° publication PCT/PCT Publication No.: 2007/100750
(30) Priorité/Priority: 2006/02/24 (US60/776,372)

(51) Cl.Int./Int.Cl. *B01D 19/00* (2006.01)

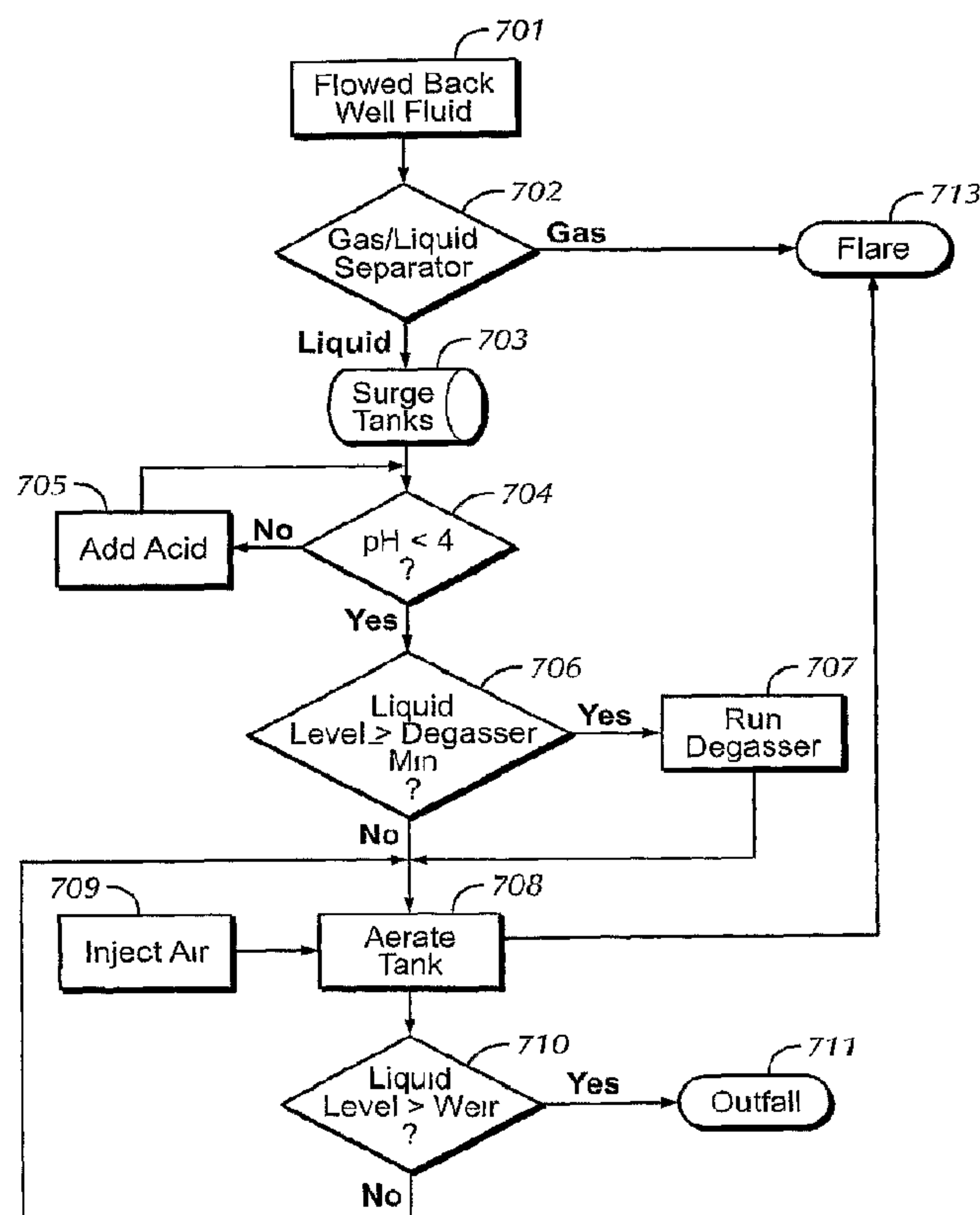
(72) Inventeurs/Inventors:
FREEMAN, MICHAEL A., US;
HAND, ERIC, US

(73) Propriétaire/Owner:
M-I LLC, US

(74) Agent: SMART & BIGGAR

(54) Titre : DEGAZEUR AERE

(54) Title: AERATED DEGASSER



(57) Abrégé/Abstract:

The present invention provides a system for reducing entrained and dissolved gasses from a well fluid. The system includes a well fluid, at least one process tank into which the well fluid flows, wherein a first process tank comprises a weir arrangement over which the well fluid spills, a mechanical degasser coupled to the at least one process tank and configured to receive the well fluid, and an aeration device disposed in the at least one process tank that generates bubbles in the well fluid. The present invention also provides a method of reducing entrained and dissolved gases from a well fluid that includes flowing a well fluid into a process tank, exerting a centrifugal force on the well fluid, and generating bubbles in the well fluid in the process tank.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
7 September 2007 (07.09.2007)

PCT

(10) International Publication Number
WO 2007/100750 A3(51) International Patent Classification:
B01D 19/00 (2006.01)(21) International Application Number:
PCT/US2007/004894(22) International Filing Date:
23 February 2007 (23.02.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/776,372 24 February 2006 (24.02.2006) US(71) Applicant (for all designated States except US): **M-I LLC**
[US/US]; 5950 North Course Drive, Houston, TX 77072 (US).

(72) Inventors; and

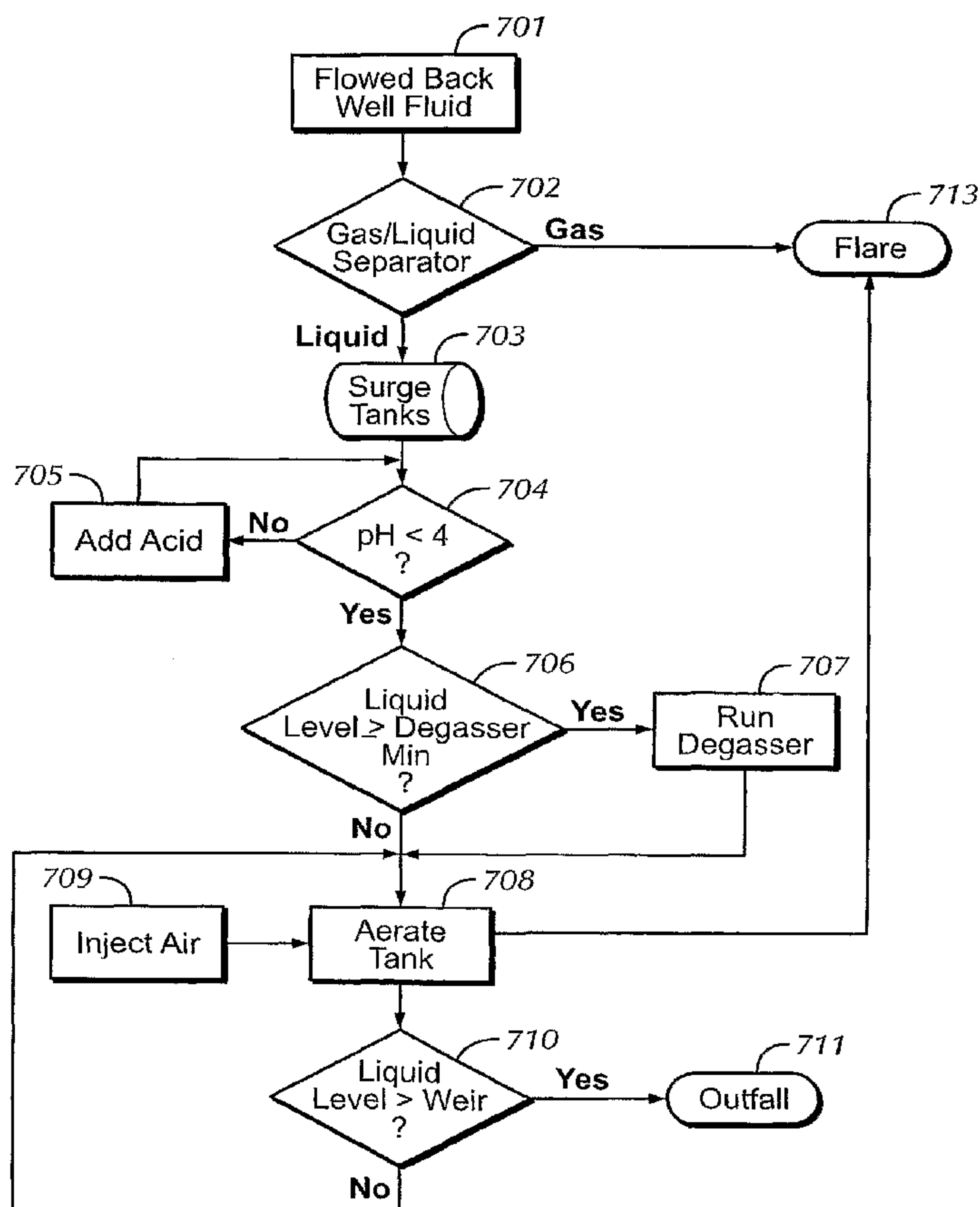
(75) Inventors/Applicants (for US only): **FREEMAN, Michael, A.** [US/US]; 3107 Greenwood Glen Dr., Kingwood, TX 77345 (US). **HAND, Eric** [US/US]; 5950 North Course Drive, Houston, TX 77072 (US).(74) Agents: **BERGMAN, Jeffrey, S.** et al.; Osha Liang LLP, 1221 McKinney St., Suite 2800, Houston, TX 77010 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: AERATED DEGASSER



(57) Abstract: The present invention provides a system for reducing entrained and dissolved gases from a well fluid. The system includes a well fluid, at least one process tank into which the well fluid flows, wherein a first process tank comprises a weir arrangement over which the well fluid spills, a mechanical degasser coupled to the at least one process tank and configured to receive the well fluid, and an aeration device disposed in the at least one process tank that generates bubbles in the well fluid. The present invention also provides a method of reducing entrained and dissolved gases from a well fluid that includes flowing a well fluid into a process tank, exerting a centrifugal force on the well fluid, and generating bubbles in the well fluid in the process tank.

WO 2007/100750 A3

WO 2007/100750 A3



Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(88) Date of publication of the international search report:

1 November 2007

AERATED DEGASSER

BACKGROUND OF INVENTION

Field of the Invention

[0001] The invention relates generally to a system for treating well fluids.

Background Art

[0002] When drilling or completing wells in earth formations, various fluids typically are used in the well for a variety of reasons. Common uses for well fluids include: lubrication and cooling of drill bit cutting surfaces while drilling generally or drilling-in (*i.e.*, drilling in a targeted petroleum bearing formation), transportation of “cuttings” (pieces of formation dislodged by the cutting action of the teeth on a drill bit) to the surface, controlling formation fluid pressure to prevent blowouts, maintaining well stability, suspending solids in the well, minimizing fluid loss into and stabilizing the formation through which the well is being drilled, fracturing the formation in the vicinity of the well, displacing the fluid within the well with another fluid, cleaning the well, testing the well, implacing a packer fluid, abandoning the well or preparing the well for abandonment, and otherwise treating the well or the formation.

[0003] In drilling some subterranean formations, and particularly those bearing oil or gas, hydrogen sulfide accumulations are frequently encountered. The circulation of well fluid brings the hydrogen sulfide from the formation to the surface. Such sulfide in the well fluid is problematic, as it can corrode the steel in the drilling apparatus and may be liberated into the atmosphere as toxic sulfide gas at the well surface. Further, hydrogen sulfide contaminated oil from the well fluid may become associated with or absorbed to the surfaces of the cuttings that are removed from the formation being drilled. The cuttings are then an environmentally hazardous material, making disposal a problem.

[0004] Generally, to protect the health of those working with the well fluid and those at the surface of the well, conditions should be maintained to ensure that the concentration of hydrogen sulfide released from the fluid, emitted due to the partial

pressure of the gas, is less than about 15 ppm. The partial pressure of hydrogen sulfide at ambient temperatures is a function of the concentration of sulfide ions in the fluid and the pH of the fluid. To ensure that the limit of 15 ppm is not exceeded even for the maximum sulfide concentration that may be encountered in a subterranean formation, the pH of the well fluid is typically maintained at a minimum of about 11.5. Also, to prevent the soluble sulfide concentration in the well fluid from becoming excessive, action is routinely taken to remove sulfide from the well fluid.

[0005] Dissolved gases cause many problems in the oil field. Gases and other fluids present in subterranean formations, collectively called reservoir fluids, are prone to enter a wellbore drilled through the formation. In many cases, dense drilling fluids, completion brines, fracturing fluids, and so forth are provided to maintain a countering pressure that restrains the reservoir fluids from entering the wellbore. However, there are many instances where the counter pressure is too low to restrain the reservoir fluids. This may be due to, for example, a mis-calculation of the fluid density needed to maintain a hydrostatic overbalance or a transient lowering of pressure due to movement of the drill string in the hole. Gasses may also enter the wellbore through molecular diffusion if there is insufficient flux of fluid from the wellbore to keep it swept away. Finally, reservoir fluids escape from the fragments of the formation that are being drilled up. The reservoir fluid that enters the well is then free to mix with the supplied well fluid and rise to the surface.

[0006] The hazards of un-restrained expansions of reservoir fluids in the wellbore are well known. A primary hazard is an avalanche effect of gas evolution and expansion, wherein gas bubbles rise in a liquid stream, expanding as they rise. As the bubbles expand, they expel dense fluid from the bore, and further reduce the hydrostatic pressure of the wellbore fluid. Such a progression may eventually lead to a 'blow out,' whereby so much restraining pressure has been lost that the high pressure reservoir can flow uncontrollably into the wellbore.

[0007] Less dramatic, but equally important, are chemical effects that formation fluids may have upon the circulating fluid, the structure of the well, and the associated personnel. These effects and risks may include, for example: methane gas liberated at the surface may ignite; carbon dioxide may become carbonic acid,

a highly corrosive compound, when exposed to water; carbon dioxide gas is an asphyxiant; hydrogen sulfide can corrode ferrous metals, particularly in contact with water, and is more damaging than carbon dioxide because it can induce hydrogen embrittlement; embrittled tubulars may separate or break well under design stresses with catastrophic consequences; hydrogen sulfide gas is also toxic, with levels of 800 to 1000 ppm causing death in healthy individuals. Removing dissolved and entrained gases is thus vital to many aspects of successful drilling and exploitation.

[0008] Chemical processes have been previously used to ameliorate the effects of dissolved gasses, particularly of hydrogen sulfide and carbon dioxide. Caustic and similar high-pH materials, for example, sodium hydroxide, are added to circulating well fluid to maintain pH. Copper, zinc, and iron compounds have been added to react with and sequester hydrogen sulfide, although they often have deleterious effects on circulating fluid properties and can cause environmental disposal issues. Oxidants, such as hypochlorite, have also been proposed, but they may have destructive effects on organic and metal components.

[0009] Accordingly, there exists a need for a method and apparatus to facilitate the removal of entrained and dissolved gases in a well fluid. Further, there exists a need for a method and apparatus to facilitate the destruction and removal of hydrogen sulfide in a well fluid.

SUMMARY OF INVENTION

[0010] In one aspect, the invention relates to a system for reducing entrained and dissolved gases from a well fluid including a well fluid, at least one process tank into which the well fluid flows, wherein a first process tank comprises a weir arrangement over which the well fluid spills, a mechanical degasser coupled to the at least one process tank and configured to receive the well fluid, and an aeration device disposed in the at least one process tank that generates bubbles in the well fluid.

[0011] In another aspect, the invention relates to a method of reducing entrained and dissolved gases from a well fluid, the method including flowing a well fluid into a

process tank, exerting a centrifugal force on the well fluid, and generating bubbles in the well fluid in the process tank.

[0012] In another aspect, the invention relates to a system for reducing entrained and dissolved gases from a well fluid including a well fluid, at least one process tank into which the well fluid flows, wherein a first process tank comprises a weir arrangement over which the well fluid spills, a mechanical degasser coupled to the at least one process tank and configured to receive the well fluid, and means for generating bubbles in the well fluid.

[0013] Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

[0014] FIG. 1 shows a hose configuration in accordance with an embodiment of the invention.

[0015] FIG. 2 shows a hose configuration in accordance with an embodiment of the invention.

[0016] FIG. 3 shows a chart of air injection rates against length of time in accordance with an embodiment of the invention.

[0017] FIG. 4 shows a system diagram in accordance with an embodiment of the invention.

[0018] FIG. 5 shows a chart of amount of hydrogen sulfide reduced with respect to pH in accordance with an embodiment of the invention.

[0019] FIG. 6 shows a system diagram in accordance with an embodiment of the invention.

[0020] FIG. 7 shows a flow diagram of a degassing system in accordance with an embodiment of the invention.

[0021] FIG. 8 shows a chart of amount of hydrogen sulfide with respect to time of in accordance with an embodiment of the invention.

[0022] FIG. 9 shows a chart of amount of hydrogen sulfide reduced with respect to time in accordance with an embodiment of the invention.

- [0023] FIG. 10 shows a chart of amount of hydrogen sulfide reduced with respect to time in accordance with an embodiment of the invention.
- [0024] FIG. 11 shows a chart of amount of hydrogen sulfide reduced with respect to time in accordance with an embodiment of the invention.
- [0025] FIG. 12 shows a chart of amount of hydrogen sulfide reduced with respect to time in accordance with an embodiment of the invention.
- [0026] FIG. 13 shows a chart of amount of hydrogen sulfide reduced with respect to time in accordance with an embodiment of the invention.
- [0027] FIG. 14 shows a chart of amount of hydrogen sulfide reduced with respect to time in accordance with an embodiment of the invention.
- [0028] FIG. 15 shows a chart of amount of hydrogen sulfide reduced with respect to time in accordance with an embodiment of the invention.

DETAILED DESCRIPTION

- [0029] In one aspect, embodiments of the invention are directed to a novel system and method for removing entrained and/or dissolved gases from a well fluid. In another aspect, embodiments of the invention are directed to a novel system and method for removing hydrogen sulfide, H_2S , from well fluids. Embodiments of the invention include both physically removing the entrained and/or dissolved gas for flaring and chemical conversion of the gas into non-toxic, non-corrosive forms. Embodiments of the invention include removal or destruction of H_2S through at least three processes, including partition of the H_2S between gas and liquid phases, acid/base equilibria between dissolved sulfide species, and electrochemical equilibria between dissolved H_2S , oxygen (O_2), sulfur (S), and water (H_2O). Embodiments of the present invention involve degassing and aeration apparatuses. Exemplary apparatuses are described below.

[0030] Degasser

- [0031] Degassers assist in maintaining a circulating fluid density so as to maintain needed hydrostatic pressure of the well fluid. A degasser applies a vacuum to a fluid and subjects the fluid to centripetal acceleration. The fluid is then sprayed against a surface, thereby removing entrained air and slowly-evolving bubbles of

dissolved formation gases from the circulating fluid before its return downhole or before the fluids disposal.

[0032] Thus, in certain embodiments a mechanical degasser, for example, a MI SWACO® CD-1400, available from M-I, LLC (Houston, TX) may be coupled to a process tank. The well fluid passes through the mechanical degasser wherein centrifugal force is exerted on the well fluid. The centrifugal force of the mechanical degasser multiplies the force acting on the entrained gas bubbles, for example, hydrogen sulfide, to increase buoyancy of the gas bubbles, thereby releasing the entrained gas bubbles from the well fluid. The increase in buoyancy of the gas bubbles accelerates the bubble-rise velocity. As the bubbles rise toward the surface, they escape the well fluid. One of ordinary skill in the art will appreciate that any device known in the art that will exert a centrifugal force on the fluid may be used in place of a mechanical degasser.

[0033] Aeration

[0034] Sparging air through liquids strips both super-saturated and sub-saturated dissolved gases by carrying them out of the liquid. If the dissolved gas is not present in the gas used to sparge, the partial pressure of the dissolved gas is accordingly zero. Thus, the dissolved gases partition into the introduced, or sparged, gas bubble. With sparging at a constant rate under conditions of vapor/dissolved gas equilibrium, the reduction of dissolved gas proceeds exponentially, limited only by the total volume of sparge gas. The volume of dissolved gas removed from the fluid, in many instances, is limited by the rate in which the sparge gas bubbles can rise through the fluid and emerge. Attempts to pump high volumes of sparge gas become frustrated as the bubble content increases, because the viscosity of the bubble/liquid system increases, thereby hindering the rise of bubbles.

[0035] The rate of oxygen transfer across the air/fluid interface can only be determined empirically. For a fixed volume of air sparged through a fluid, mass transfer of gases into and out of the fluid is be a strong function of the surface area at the air/gas interface. Further, the more time each bubble resides in the liquid, the more complete the exchange. The Stokes-Einstein equation shows that residence time is primarily a function of the bubble diameter, gross density of the

media, and system viscosity. The Stokes-Einstein equation may be written $D = kT/f$ where D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, and f is the frictional coefficient, wherein $f = 6\pi a\eta$, where a is the radius of a particle and η is the viscosity of a solvent. Small bubbles have larger surface area per volume and rise more slowly as compared to larger bubbles. Additionally, at higher concentrations, small bubbles will viscosify a fluid. Accordingly, a high volume fraction of small bubbles will provide greater reaction with hydrogen sulfide than a low volume fraction of large bubbles. "Small" and "large", as used herein with reference to the bubble, are relative to the rate at which the bubbles rise in a given system under a given set of conditions including rate of air injection, temperature, fluid viscosity, etc.

[0036] Bubbles may be generated by any method known in the art. For example, bubbles may be generated by an aeration device. In one embodiment the aeration device may include a septum or membrane configured with small perforations through which air may be released. In one embodiment, the membrane may be flexible, such as a woven or non-woven fabric, or a sheet of rubber or other elastomer with perforated openings cast or otherwise formed there-through. Alternatively, the membrane may be rigid, for example a solid frit, which is a body of sintered particles with fine openings between particles, or a metal surface with fine perforations, or openings devised by any means known in the art. Examples of such commercially available porous septa and perforated media are given in, for example, Chapter 18 of Perry's Chemical Engineers' Handbook, 6th ed (1984). Further, bubbles may be created by passing gas through a surface free of openings, such as permeating hydrogen through a palladium film, at a lower flux. One of ordinary skill in the art will appreciate, however, that the membrane may be constructed of any of a number of materials known in the art, for example, glass, metal, plastic, etc., such that air may be sparged into the fluid. Bubbles may also be generated through direct mechanical means, wherein air is entrained in a well fluid by mixing. Further, bubbles may be generated through chemical means by various reactions known in the art that may convert solid or liquid components into gases.

[0037] In another embodiment, bubbles may be generated through destabilizing a gas-liquid solution. Bubbles may spontaneously form when the pressure or

77680-67

temperature of a liquid is changed from a previous state of gas/liquid saturation. Commercially, Dissolved Air Flotation (DAF) saturates water with air at higher applied pressure, for example, 100 psi, and then reduces the pressure of the system. The water may then be allowed to flow from a closed pressured conduit or vessel into a large vessel open to the atmosphere. Several commercial devices and processes for generating bubbles by destabilizing a gas-liquid solution are cited in Perry's Chemical Engineers' Handbook, 6th ed (1984).

[0038] In one embodiment, bubbles may be generated proximate an intake of a degasser. In one embodiment, a flexible, porous hose may sparge air into a fluid. The flexible, porous hose may be attached to weighted frames by any method known in the art, for example, by plastic ties or wire wrap. The hose may be fashioned into any shape using standard hose fittings. In one embodiment, the hose may be disposed proximate the intake of a degasser. Figure 1 shows an example of a hose 101 configured with small perforations 102 to introduce bubbles proximate the intake of a degasser. While the circular hose of Figure 1 provides short air/water contact times, it minimizes the opportunities for foaming, thereby reducing the risks involved in introducing air into a fluid. In another embodiment, shown in Figure 2, a more aggressive air injection may be provided using a bubbler pattern that covers the entire base of the process tank. A hose 201 may be secured to a weighted frame 203. Such an arrangement provides more linear feet of the hose, or bubbler, and many more bubbles for a given process tank. For a hose that covers the entire base of a tank, many of the bubbles generated may be outside the immediate draw of the degasser. In this embodiment, the degasser used must be effective to reduce foaming.

[0039] In order to maintain the integrity of the porous hose and the proper bubble size, a proper range of air bubbles introduced into the fluid may be determined by measuring flow rate of the air as a function of hose length and applied pressure, as shown in the Examples below.

[0040] To determine the bubble size and volume fraction of bubbles, empirical testing was done using an open, rectangular tank with a degasser unit, for example, MI SWACO® CD-1400, mounted in the process tank. In this test, the process tank was filled with potable water to within 17 and 5/8 inches of the top, that is 1700

gal (6.4 m³) of water. A circular hose, shown in Figure 1, introduced bubbles at the base of the degasser.

[0041] Figure 3 shows the resulting air injection rates achievable for varied lengths of soaker hose for a range of injection pressures. Fine bubble generation was limited to injection pressures of 25 psi or lower. For shorter hose lengths, the air injection rate was limited due to over-pressuring of the hose. Accordingly, longer lengths of tubing are required to achieve high flow rates at low injection pressures. Thus, in this embodiment, approximately 50L/min of air per meter of hose is required to retain fine bubble generation.

[0042] **Thermodynamic Considerations**

[0043] Partition of the H₂S between gas and liquid phases is a kinetic process that approaches a thermodynamic equilibrium described by Henry's Law:

$$Y_i = H\chi_i \quad (1)$$

where Y_i is the partial pressure of species i over a solution, χ_i is mole-fraction of i in the solution, and H is a constant, appropriately called the Henry's law constant, unique to each species i . For H₂S, H has a value of 8.56×10^{-3} atm·m³/mol at 20°C. This relation applies to air and water in the degassing system strictly when the two phases are allowed to stand long enough in contact for all portions of the gas and liquid to come into equilibrium. For example, if pure water were allowed to stand in a atmosphere of pure H₂S, the equilibrium concentration of dissolved H₂S would be 3740 mg/L.

[0044] In one embodiment, as shown in Figure 4, air bubbles 419 are injected into a well fluid 420 contained in process tank 422. Entrained gases, for example hydrogen sulfide, may escape and fill the headspace volume 424. The gases that fill the headspace volume 424 are sent to flare 426.

[0045] In one embodiment, water containing dissolved H₂S may flow into a process tank with the following system limitations. The equilibrium concentration of H₂S in the air space of the process tank may be determined as described below. In one example, a process tank may have a total volume of 8,000 L and may be loaded with 6,000L of water containing 1,000 mg/L of H₂S. This leaves 2,000 L of vapor space. The air in the vapor space may be void of oxygen (for reasons discussed later). In

this example, the pH is kept stable at 2.0 even as H₂S leaves the fluid. The following table summarizes the initial conditions of the system.

Table 1

H ₂ S in Water (mg/L)	1000
H ₂ S in Air (ppm by volume)	0
Volume of static air (L)	2,000
Volume of static water (L)	6,000
pH	2.0

[0046] The 6,000 L of water contains (1,000 mg/L x 6,000 L x 1g/1000mg x 1kg/1,000g) 6 kg of H₂S. The molecular weight of H₂S is approximately 34 g/mol, so there are (6 kg x 1000g/kg x 1 mol/34 g) 176.47 mol of H₂S in the water.

[0047] Neglecting the very small amount of water displaced by the gas, the mole fraction of H₂S may be calculated as (moles H₂S)/(moles water). One liter of water weighs nearly 1 kg, and the molecular weight of water is 18 g/mol. Thus, there are (1 kg x 1000g/kg x 1 mol/18 g) 55 mol/L of water. The number of moles of water can be determined by multiplying the total volume of static water by the fraction of mol/L of water (55 mol/L x 6000 L) to yield 330,000 mol of water. Accordingly, the mole fraction of H₂S is approximately (176.47/330,000) 0.000535.

[0048] The air space is initially free of H₂S, and to fill it requires that H₂S leave the liquid. This reduces the mole fraction, thereby reducing the calculated equilibrium. To solve, consider the mass balance:

$$S_T = S_A + S_L \quad (2)$$

where S_T is the total sulfur in the unit, in this case 176.5 moles (from above), S_A is the moles air space sulfur, and S_L is moles liquid phase sulfur. Accordingly, the moles air space sulfur can be written as:

$$S_A = S_T - S_L = 176.5 - S_L \quad (3)$$

[0049] To convert the moles air space sulfur, S_A , to a mole fraction gas, the ideal gas law may be used to first determine the volume of H₂S gas. Assuming a

constant temperature of 25°C, the ideal gas law may be expressed as ($PV=nRT$, RT is constant) $22.4 \text{ (L*atm/mol)*}n=PV$, where n is the number of moles, P is the pressure, and V is the volume.

$$\text{Volume H}_2\text{S} * Y_i = S_A \times 22.4 \text{ L*atm/mol};$$

[0050] Next, dividing by total volume to get the partial pressure:

$$Y_i = S_A \times 22.4 \text{ L*atm/mol} / 6,000\text{L}$$

[0051] Substituting for S_A ,

$$Y_i = (176.5 - S_L) \times 22.4 \text{ L*atm/mol} / 6,000\text{L}$$

[0052] As above, the mole fraction in the liquid is:

$$\chi_i = S_L \text{ H}_2\text{S} / 330,000 \text{ mol water}$$

[0053] Now, substituting for the variables in Henry's Law:

$$Y_i = H\chi_i$$

$$(176.5 - S_L) \times 22.4 \text{ (L*atm/mol)} / 6,000 \text{ L} = 8.56 \times 10^{-3} \text{ (atm*m}^3\text{/mol)} \times 1000 \text{ (L/m}^3\text{)} \times S_L / 330,000 \text{ mol}$$

[0054] Solving for the moles of liquid phase sulfur, $S_L = 175.68 \text{ mol}$.

[0055] And then plugging the value of S_L into Equation 3, gives S_A :

$$S_A = (176.5 - 175.2) = 1.3 \text{ mol}$$

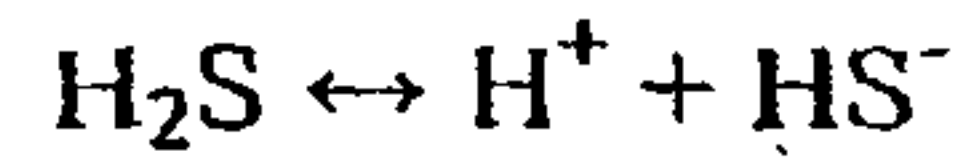
[0056] From the above, it is apparent that putting the fluid into a process tank and letting the H_2S escape does very little to reduce the H_2S content in the fluid. If the system is to be effective, there must be a much larger volume of gas into which the H_2S can escape. Because the process tank size is fixed, and cannot be pressured, volume of gas into which the H_2S can escape may only be increased by passing gas through the process tank.

[0057] **Acid/Base Equilibria**

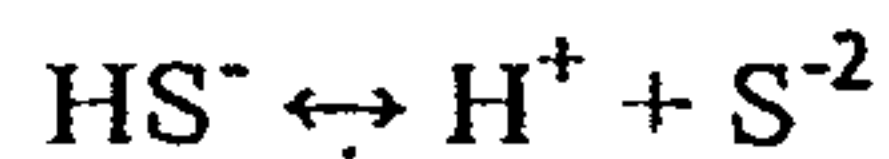
[0058] The importance of maintaining the pH of the fluid and the determination of a pH threshold for effective stripping of hydrogen sulfide from the well fluid is illustrated below.

77680-67

[0059] Hydrogen sulfide is an acid with two equivalents per mole, sequentially ionizing:



and



[0060] Hydrogen sulfide is a mild acid as shown by its acidity constants:

$$K_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad K_1 = 1.039 \times 10^{-7}$$

$$K_2 = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \quad K_2 = 6.43 \times 10^{-16}$$

[0061] The second ionization constant is relatively low or weak such that S^{2-} is virtually non-existent in dilute aqueous systems. Henry's law (shown in Equation 1) holds only when there is no chemical reaction between the solute and solvent. Accordingly, the pH of the well fluid affects the hydrogen sulfide ionization and the H_2S concentration. Thus, the liquid/gas equilibria of H_2S is partially dependent on the ionization of the hydrogen sulfide. Sulfide in the form of HS^- is not volatile. As shown in Figure 5, as the pH falls below 6, the sulfide in the well fluid is more likely to be in the non-volatile, HS^- , form. In one embodiment, a buffer may be added to the fluid to maintain a pH of less than 6. For example, citric acid may be provided to hold the pH at 4.

[0062] Electrochemical Equilibria

[0063] In one embodiment, oxygen is sparged into the well fluid to remove hydrogen sulfide from the well fluid. Oxygen in the sparged air, generally a nuisance to well fluids in the wellbore because of its corrosive nature, can be beneficial in sparging operations of general fluids. Hydrogen sulfide reacts with oxygen to become relatively harmless elemental sulfur. U.S. Patent No. 5,525,242 issued to Kerecz and U.S. Patent No. 6,352,943 issued to Kohlenberg describe methods of removing hydrogen sulfide by sparging with air. Additionally, the removal of air may be facilitated by dispersing the water as a mist or inducing a vortex.

[0064] While nitrogen may be used in sparging processes, oxygen is a more effective sparging agent for scavenging hydrogen sulfide, because oxygen readily reacts with hydrogen sulfide. The thermodynamic drive to convert elemental oxygen into water by reacting with hydrogen sulfide to form elemental sulfur results in very low residual hydrogen sulfide. The kinetics of oxygen transfer across the gas/liquid interface may be a limiting factor; however, by using small bubbles rather than larger bubbles (as discussed below), this process may become more effective. The determination of how large a contribution oxygen makes to the removal of hydrogen sulfide in the well fluid is detailed below.

[0065] Air oxidation takes place via the reaction:



[0066] A one-sided arrow is used to indicate the reaction goes in only one direction, because the equilibrium between the products and reactants is very large. The equilibrium is written:

$$K_{eq} = \frac{[S^0][H_2O]}{[H_2S][O_2]}$$

[0067] The value of K may be determined by the Nernst equation:

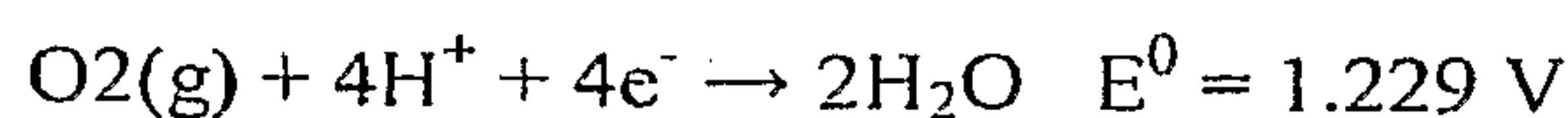
$$E = E^0 - \frac{RT}{nF} \log \left(\frac{[S^0][H_2O]}{[H_2S][O_2]} \right) \quad (5)$$

where E is the maximum potential difference, or electromotive force, R is the thermodynamic gas constant, T is the absolute temperature, F is Faraday's constant, and n is the number of electrons. At 25°C, 0.0592 V may replace RT/F in Equation 5 above.

[0068] The overall reaction may be written as:



[0069] The half-cell reactions and corresponding oxidation potentials of the oxidation reaction shown in Equation 6 are:



[0070] Therefore, the potential of the overall reaction is $(1.229 - 0.142) 1.077$. The number of electrons, n , is 4. Plugging these values back into the Nernst Equation (Equation 5) yields:

$$\text{Log}_{10}K = 4 \times 1.077/0.0592 \cong 72 \quad K \cong 10^{72}$$

[0071] Accordingly, essentially all of the oxygen is consumed with concomitant destruction of hydrogen sulfide.

[0072] Process Overview

[0073] In one embodiment, a system for removing hydrogen sulfide is shown in Figure 6. H_2S enters the system as soluble sulfides with well fluid 630 as it is flowed into process tank 632. The well fluid 630 pours into the process tank until it reaches a pre-selected depth corresponding to a pre-selected volume. For example, in one embodiment, the pre-selected depth corresponds to a volume of 6 m^3 of contained well fluid. Air 634 is sparged into the fluid 630. A mechanical degasser (not shown) coupled to the process tank 632 exerts a centrifugal force on the well fluid 630 to facilitate the escape of entrained gases into headspace volume 636. The removed entrained gases are sent to flare 638 for burning. As the well fluid 630 level in the process tank 632 rises above the pre-selected depth of contained well fluid due to the input flow of well fluid and the sparged air 634, the contained well fluid 630 spills over a weir arrangement in the process tank into a separate compartment.

[0074] In one embodiment, as shown in Figure 7, a mobile degassing system is provided to remove entrained and/or dissolved gases from a well fluid. In this embodiment, a well fluid, for example, a spent acid, is flowed back 701 from the well. The well fluid undergoes a gross gas/liquid separation 702 in a unit upstream from the system, with the gases sent to a flare 713. At least one surge tank 703 regulates the flow of the well fluid before the well fluid enters a process tank containing at least one weir. The pH of the well fluid in the process tank is measured at 704. The pH of the well fluid may be measured by any method known in the art, and is not limited herein. If the well fluid has a pH greater than 4, then acid is added, shown at 705, to the well fluid until a pH of less than 4 is reached. In one embodiment, the acid added to the well fluid to maintain a pH of 4 may be

citric acid. One of ordinary skill in the art will appreciate that other acids may be used to lower and maintain the pH of the well fluid.

[0075] If the pH of the well fluid is less than 4, then the level of fluid in the process tank is measured, shown at 706. One of ordinary skill in the art will appreciate that the level of fluid in the process tank may be measured by any method known in the art, for example, electronically by a sensor or manually by a system operator. Once the liquid level has reached a predetermined value required for running a degasser, the degasser is turned on, shown at 707.

[0076] In one embodiment, the well fluid is aerated 708 by injecting or sparging air 709 through the fluid in the process tank. In one embodiment, the fluid sparged through the well fluid is oxygen. In one embodiment, the mechanical degasser and sparging are performed simultaneously. The centrifugal force of the mechanical degasser multiplies the force acting on the entrained gas bubbles and the oxygen bubbles to increase buoyancy and release of both the entrained gas bubbles and the oxygen bubbles. The increase in buoyancy of the bubbles accelerates the bubble-rise velocity. As the entrained gas bubbles and the oxygen bubbles rise toward the surface, they escape the well fluid. Additionally, the oxygen injected into the well fluid may react with hydrogen sulfide dissolved in the fluid, thereby producing elemental sulfur, which may be more easily separated from the fluid. When the well fluid rises to the level of the weir 710 due to the input flow of well fluid and aeration of the tank, the well fluid pours over the weir and empties into another containment. The outfall well fluid 711 may then be safely disposed.

[0077] The aeration and degassing system may be continuously operated for a period of time. In one embodiment, the aeration and degassing system is continuously operated for approximately 8 to 10 hours at a time. After aeration and degassing may be stopped periodically during the process to remove elemental sulfur from the process tank that results from the reaction between oxygen sparged into the well fluid and entrained hydrogen sulfide.

[0078] **Examples**

[0079] Example 1

[0080] As a first example, consider the case where no sparging occurs. Assume a total of 20m³ of well fluid having a pH of 2.0 to be treated and a feed rate of the

well fluid is 800 L/min. Initially, the well fluid flows into a process tank having a volume of 8,000L. Once 6 m³ of well fluid has poured into the process tank, the well fluid will begin to spill over the weir. The well fluid in the process tank and the well fluid that spills over the weir retain 1,000 mg/L dissolved sulfides. Accordingly, no sulfur is removed from the well fluid. Figure 8 shows the relationship between well fluid in the process tank, the well fluid that spills over the weir, and the moles of sulfur gas.

[0081] Example 2

[0082] In another example, 6,000L well fluid with a pH of 2.0 contained in a 8,000L process tank is sparged with “zero air,” that is, air that contains no oxygen, at a rate of 100 L/min. Sparging the well fluid with zero air at 100 L/min results in modest hydrogen sulfide stripping. As shown in Figure 9, spent well fluid in the process tank is continuously stripped of hydrogen sulfide, but even after 100 minutes only a level of about 580 mg/L sulfur is reached for the 6 m³ of well fluid retained in the unit.

[0083] Example 3

[0084] In another example, 6,000L of well fluid with a pH of 2.0 contained in a 8,000L process tank is sparged with zero air at a rate of 1,000 L/min. The amount of sulfur reduced over time as a result of the sparging is shown in Figure 10 for both the well fluid in the process tank and the well fluid that spills over the weir. Sparging the well fluid with zero air at 1,000 L/min results in larger reduction in sulfur content than sparging the well fluid with zero air at 100 L/min.

[0085] Example 4

[0086] In another example, 6,000L of well fluid with a pH of 2.0 contained in a 8,000L process tank is sparged with zero air at a rate of 10,000 L/min. Sparging the well fluid with zero air at 10,000 L/min results in significant and immediate reduction in sulfides, as shown in Figure 11 for both the well fluid in the process tank and the well fluid that spills over the weir.

[0087] Example 5

[0088] If the pH is raised to a pH value of 8 in the sparging system described in Example 4 above, the extraction of hydrogen sulfide is less efficient. Figure 12

shows the result of a system where the pH is 8 and zero air is sparged through the well fluid at a rate of 1,000 L/min for both the well fluid in the process tank and the well fluid that spills over the weir. A comparison between Figure 12 (pH 8) and Figure 10 (pH 2) shows the extraction of hydrogen sulfide in the higher pH well fluid is much less efficient than in the well fluid with a lower pH.

[0089] Example 6

[0090] If the well fluid in the process tank of Example 2 is sparged with oxygen, instead of zero air, at the same rate of 100 L/min, the instantaneous stripping of hydrogen sulfide does not drastically improve. However, the final amount of sulfur concentration present in the well fluid is reduced. See Figure 13.

[0091] Example 7

[0092] If the well fluid in the process tank of Example 3 is sparged with oxygen, instead of zero air, at the same rate of 1,000 L/min, the sulfur concentration present in the well fluid is significantly reduced. As shown in Figure 14, the reactions are complete in less than 40 minutes.

[0093] Example 8

[0094] If the well fluid in the process tank of Example 5 is sparged with oxygen, instead of zero air, at the same rate of 10,000 L/min, sulfur present in the well fluid is destroyed and extracted in real time, as shown in Figure 15. This example assumes perfect mass-transport across the gas/liquid interface.

[0095] Advantageously, embodiments of the present invention provide a system and method for reducing the amount of hydrogen sulfide in a well fluid. Further, embodiments of the present invention may reduce the risks to both the structure of the well and personnel associated with circulating well fluid, including embrittled tubulars, corrosion of equipment, and death.

[0096] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

77680-67

CLAIMS:

1. A method of reducing entrained and dissolved gases from a well fluid comprising:
 flowing a well fluid into a process tank;
 5 exerting a centrifugal force on the well fluid; and
 generating bubbles in the well fluid in the process tank.
2. The method of claim 1, further comprising determining the pH of the well fluid in the process tank.
3. The method of claim 2, further comprising maintaining the pH of the
 10 well fluid in the process tank below a predetermined value.
4. The method of claim 3, wherein maintaining the pH of the well fluid comprises supplying an acid to the well fluid in the process tank.
5. The method of claim 4, wherein the acid is citric acid.
6. The method of claim 1, further comprising flaring the gas.
- 15 7. The method of claim 1, wherein generating bubbles in the well fluid comprises injecting gas injected into the well fluid.
8. The method of claim 7, wherein the gas injected in the well fluid comprises oxygen.
9. The method of claim 1, wherein the exerting a centrifugal force on
 20 the well fluid is performed after the well fluid reaches a predetermined volume of the process tank.
10. The method of claim 1, further comprising spilling the well fluid in the process tank over a weir.

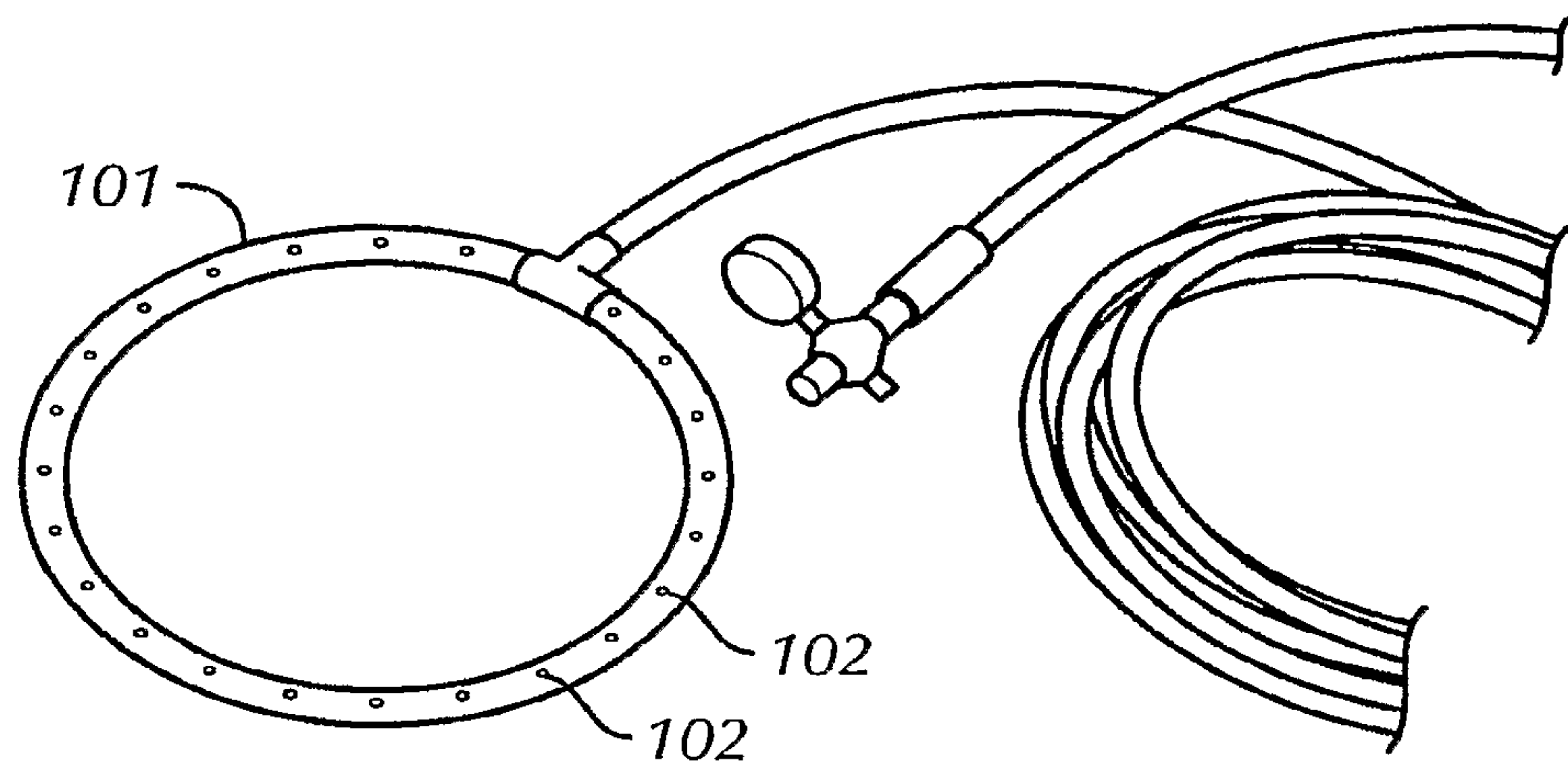
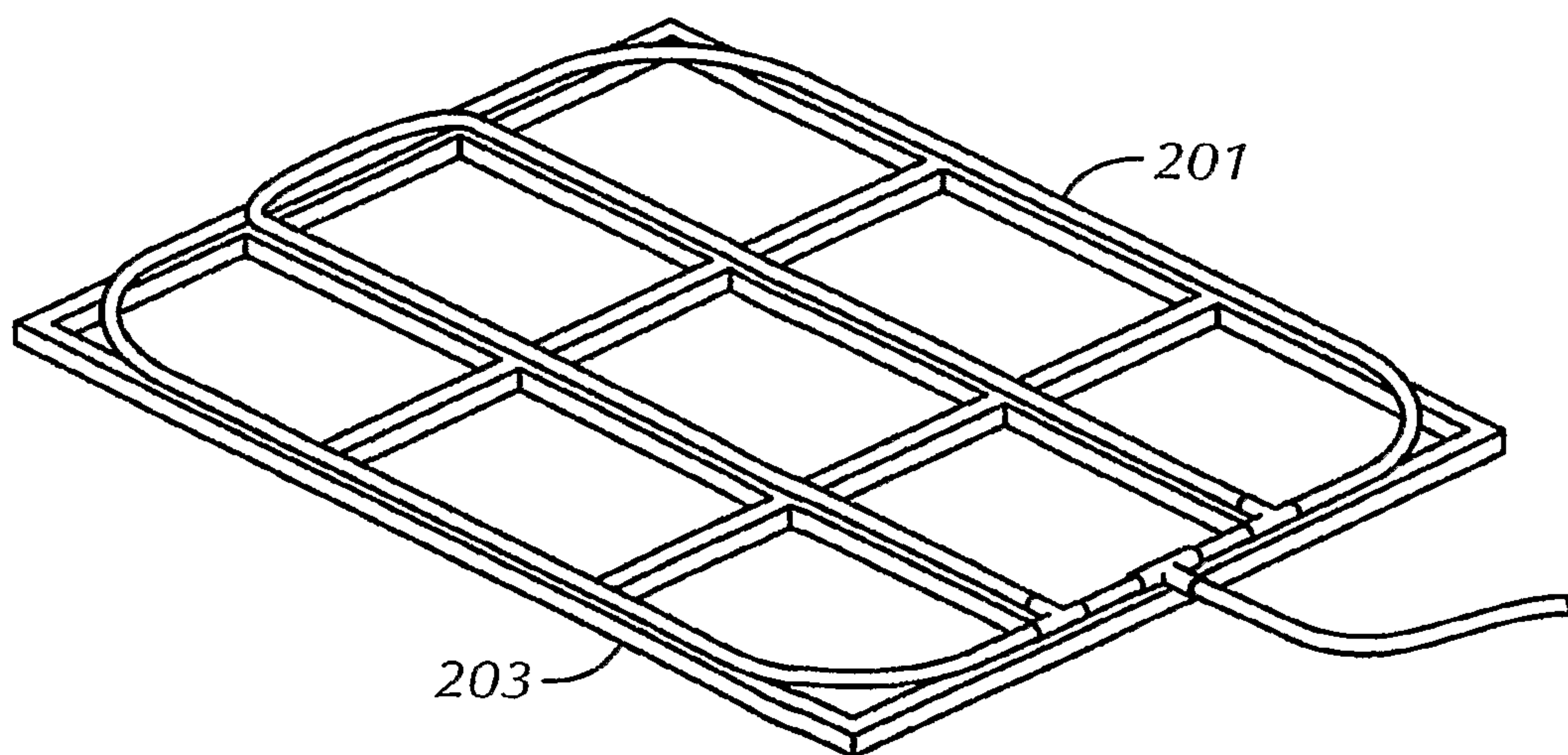
77680-67

11. The method of claim 1, wherein the generating bubbles comprises injecting air through a hose comprising at least one perforation.

12. The method of claim 11, wherein the hose comprises one selected from the group consisting of elastomer, frits, glass, metal, plastic, and any
5 combination thereof.

13. The method of claim 1, further comprising flaring gases separated from the well fluid.

14. The method of claim 1, wherein the exerting a centrifugal force on the well fluid and the injecting the air into the well fluid is performed
10 simultaneously.

1/8**FIG. 1****FIG. 2**

2/8

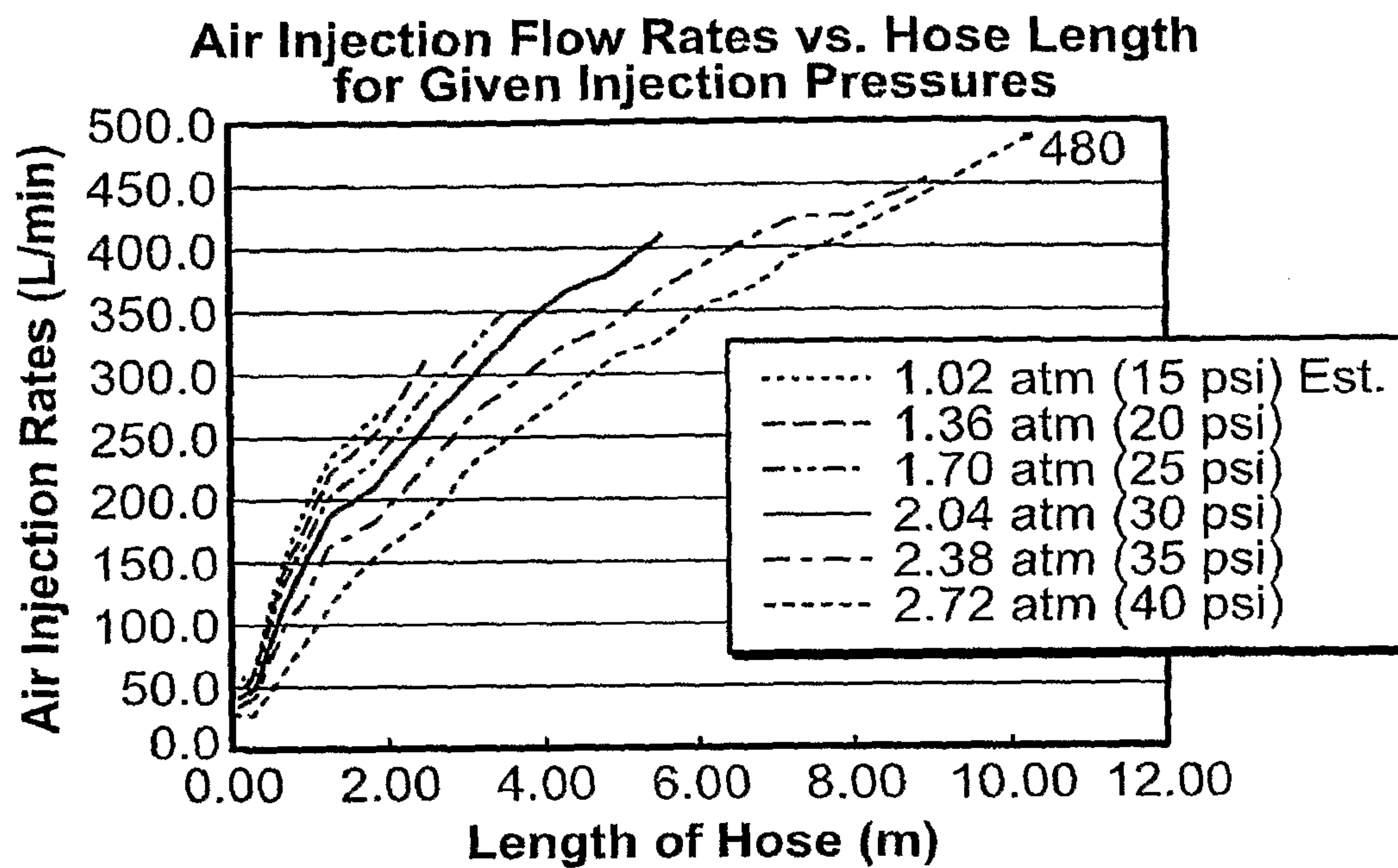


FIG. 3

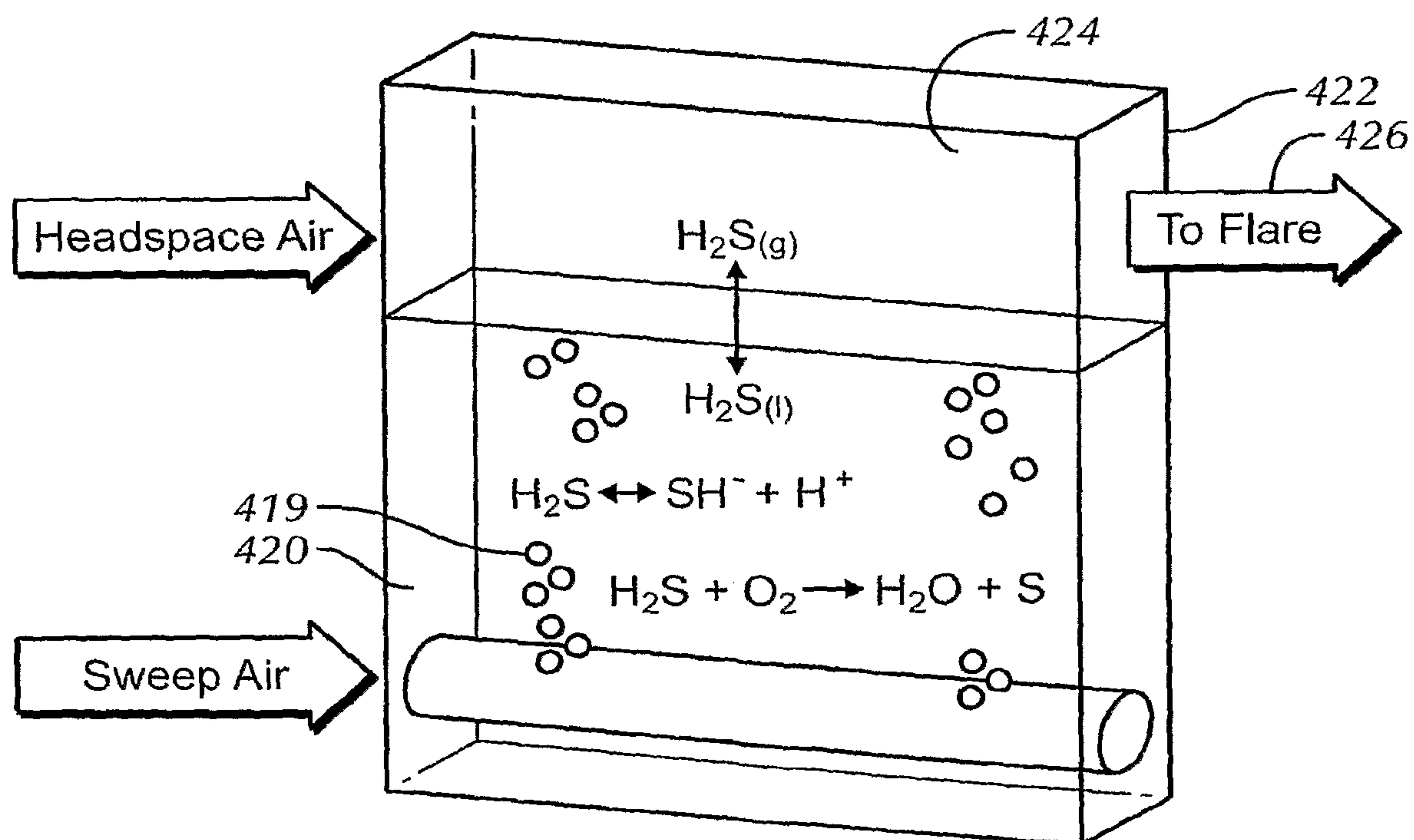
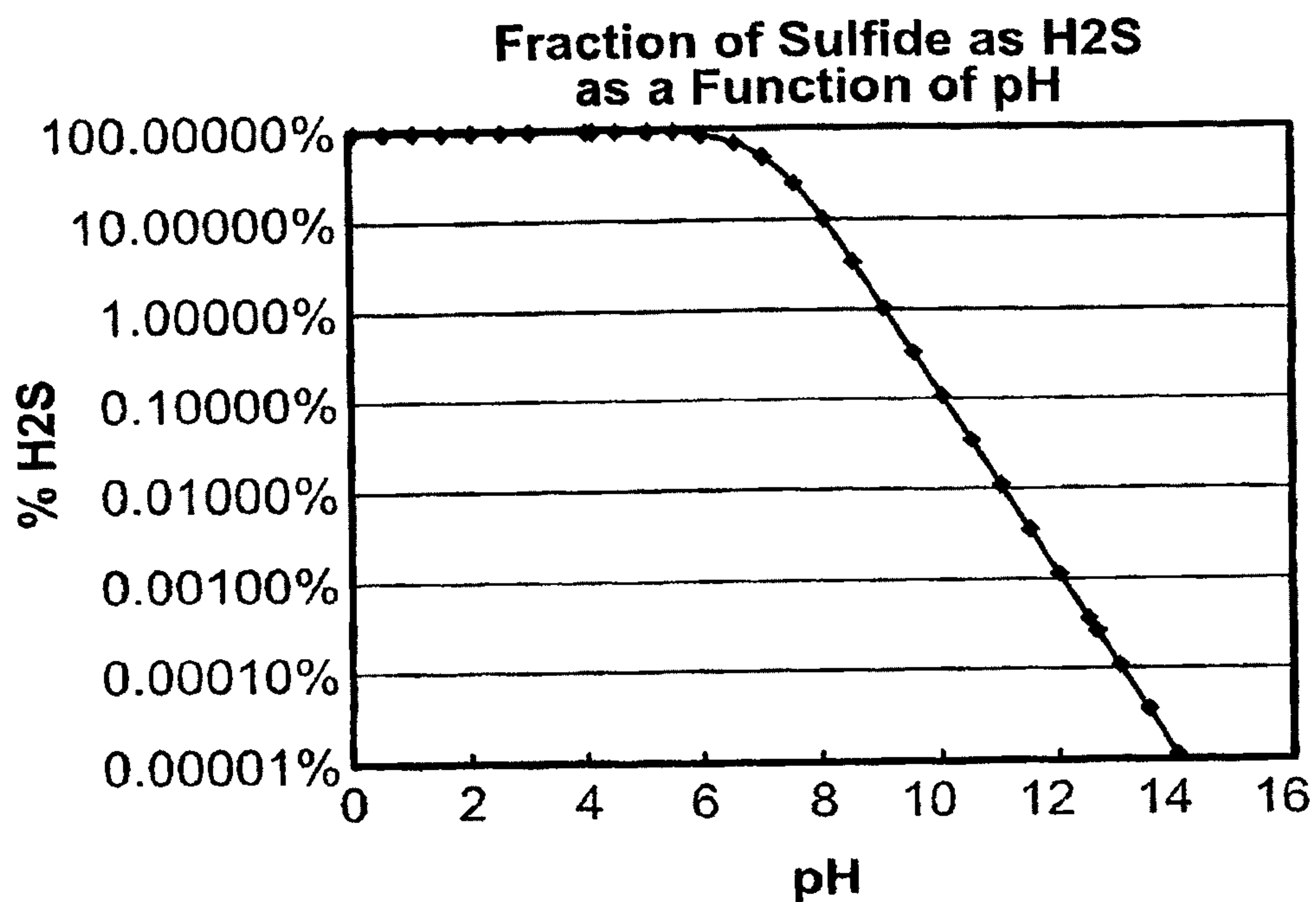
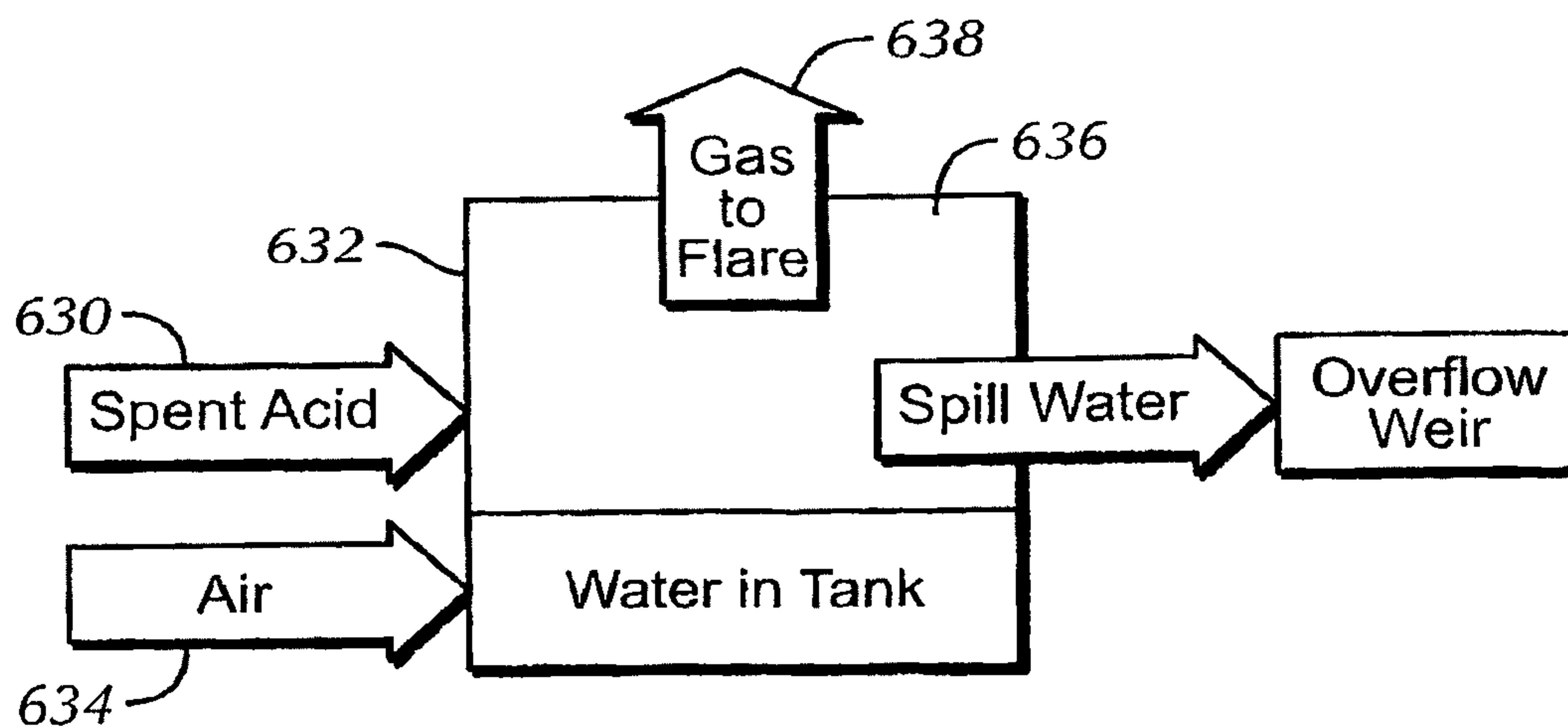


FIG. 4

3/8

**FIG. 5****FIG. 6**

4/8

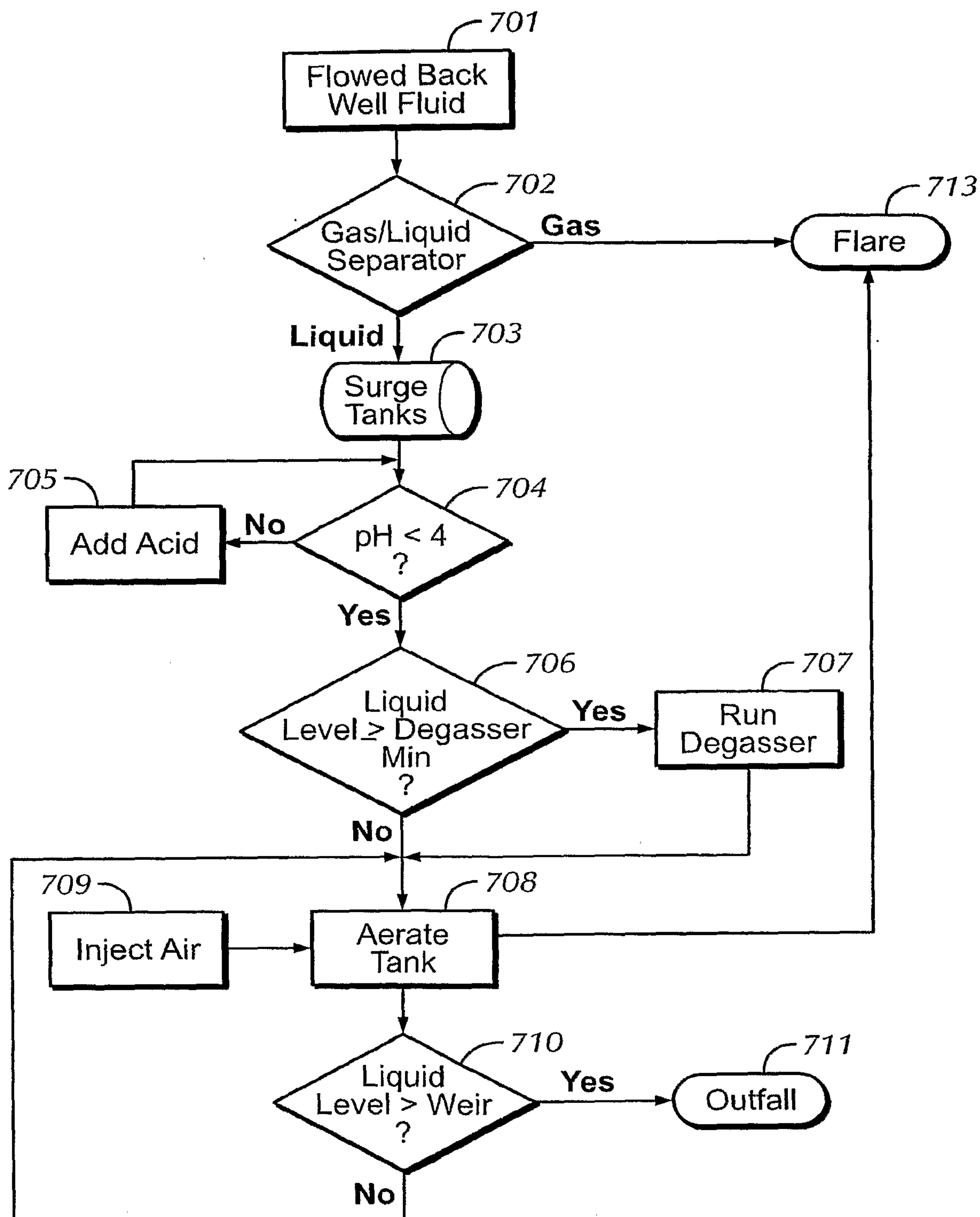


FIG. 7

5/8

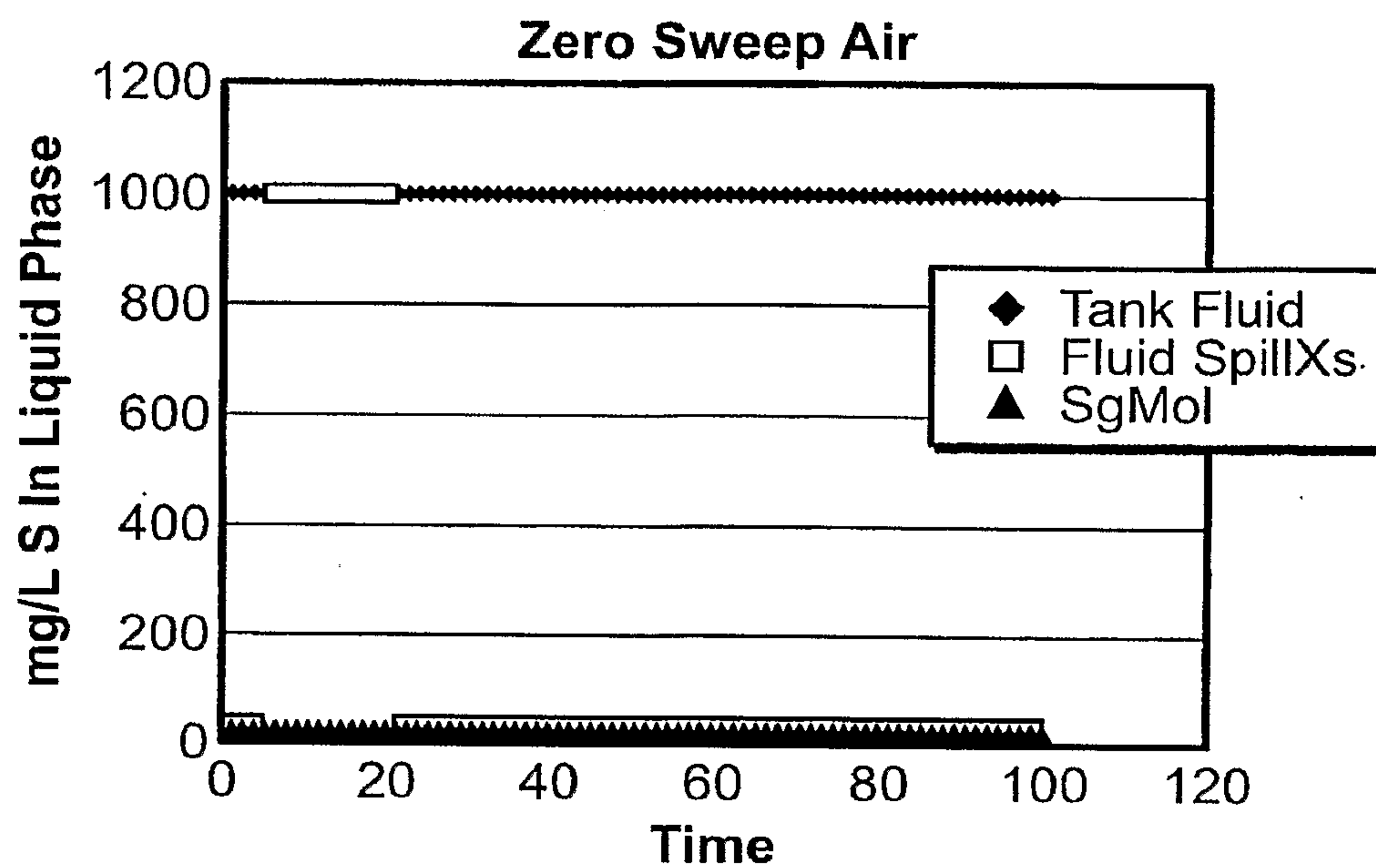


FIG. 8

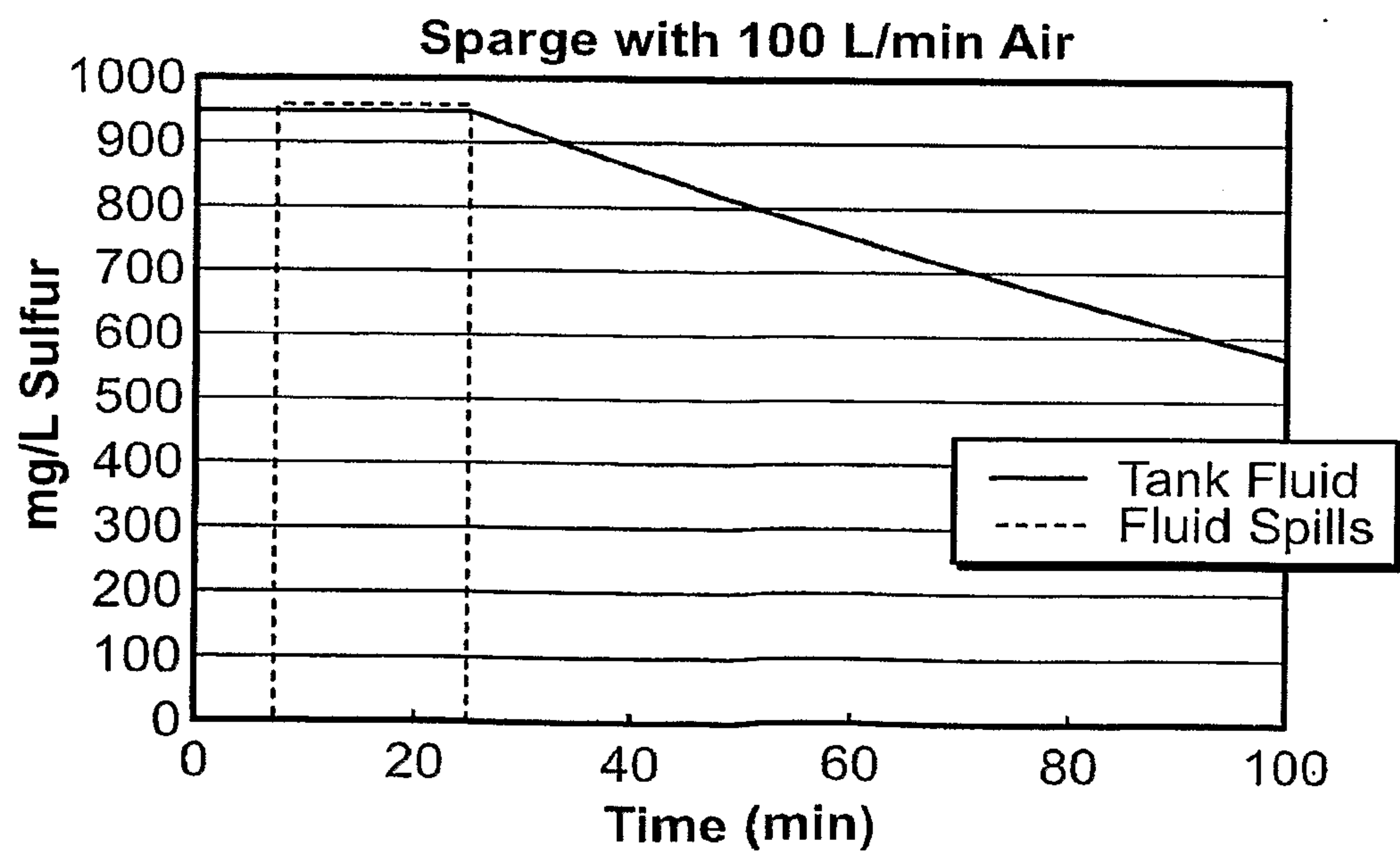
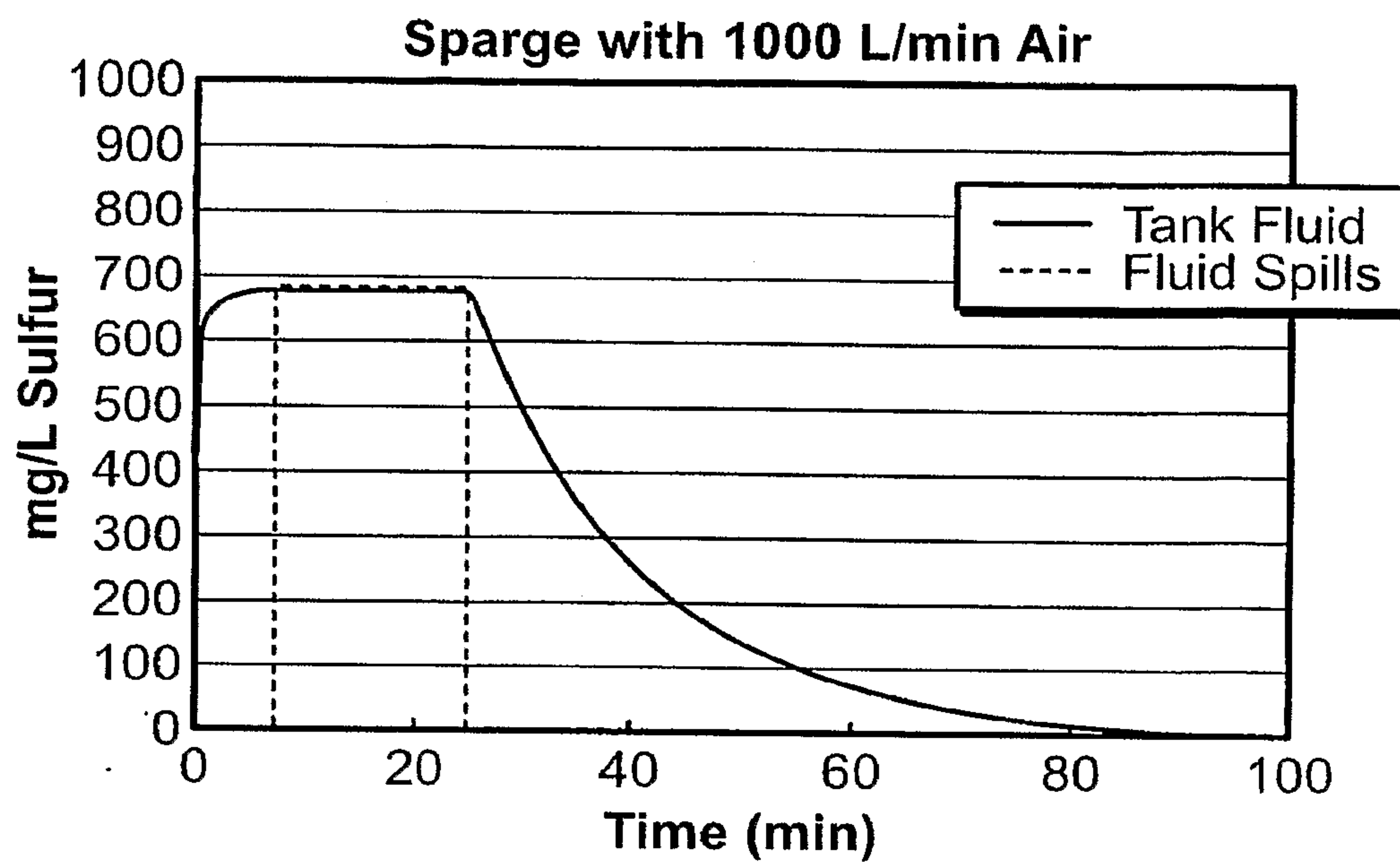
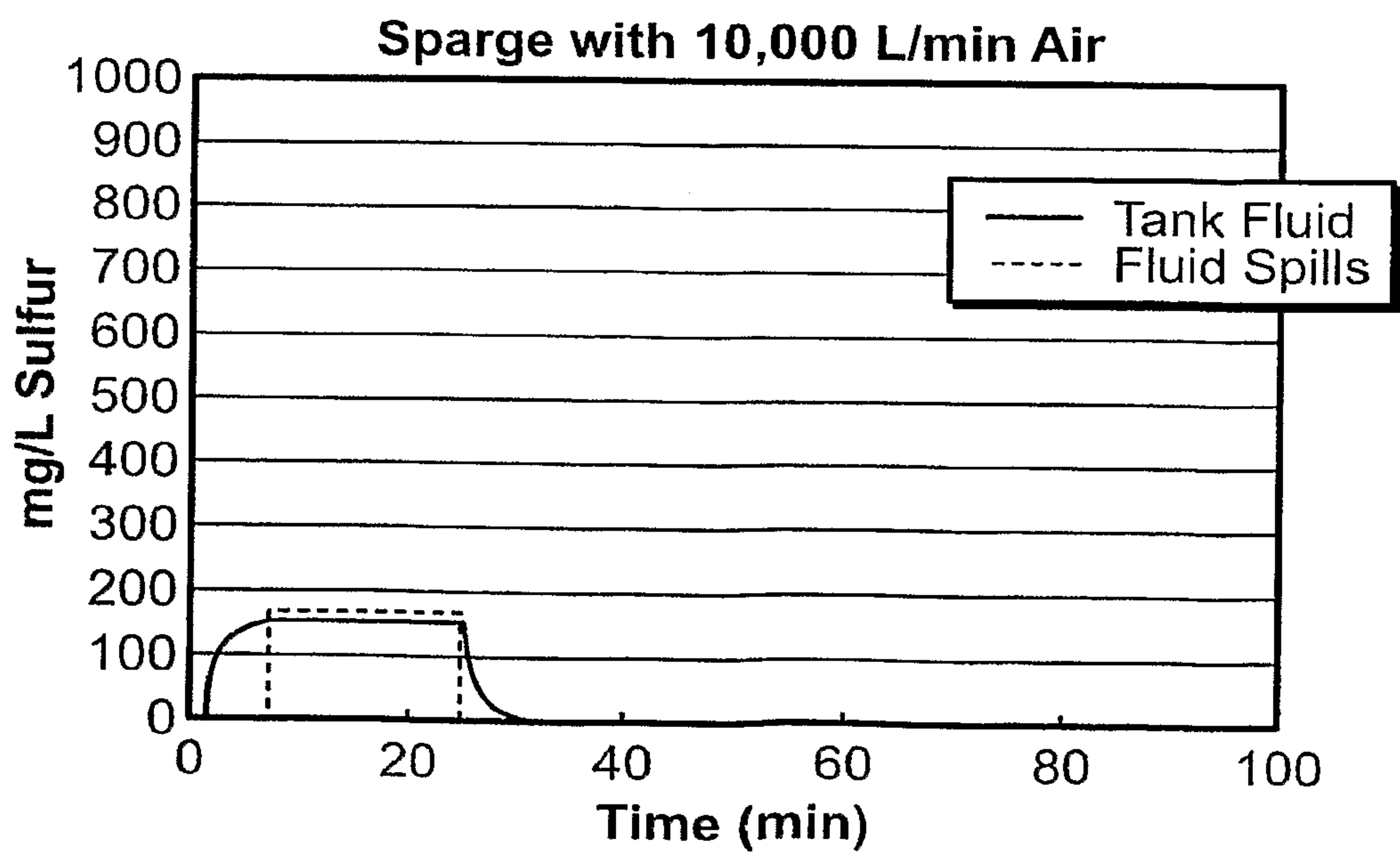
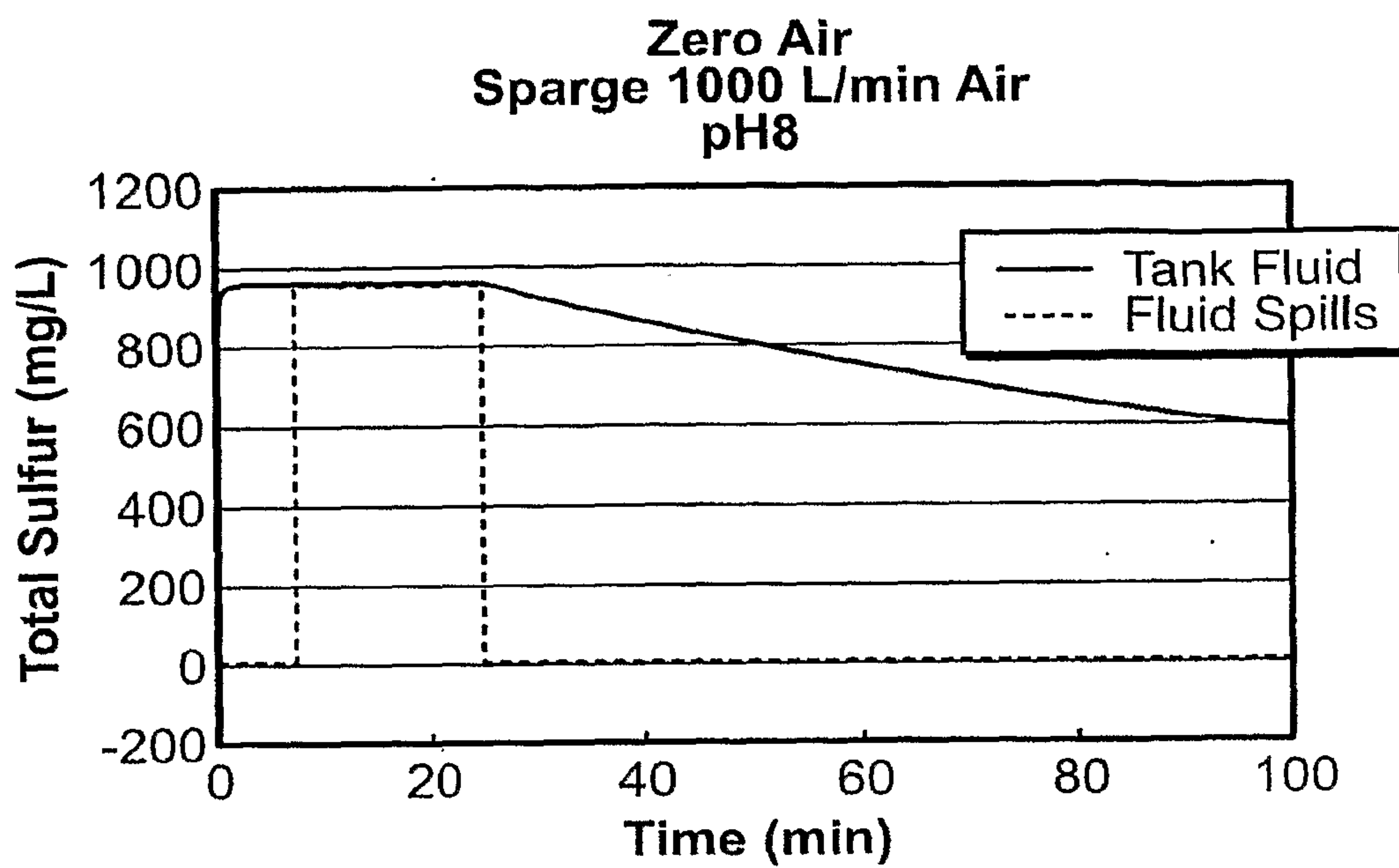
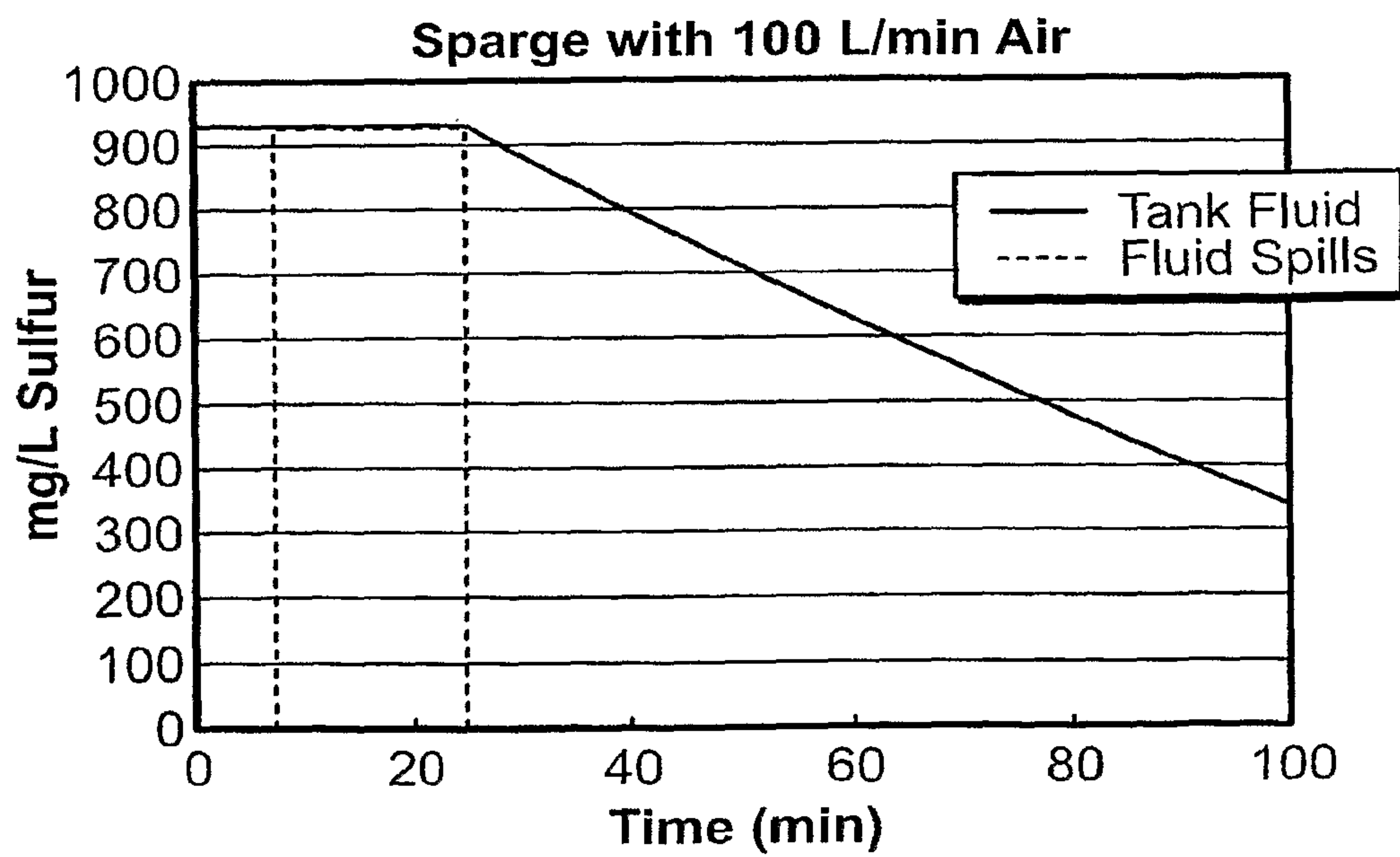


FIG. 9

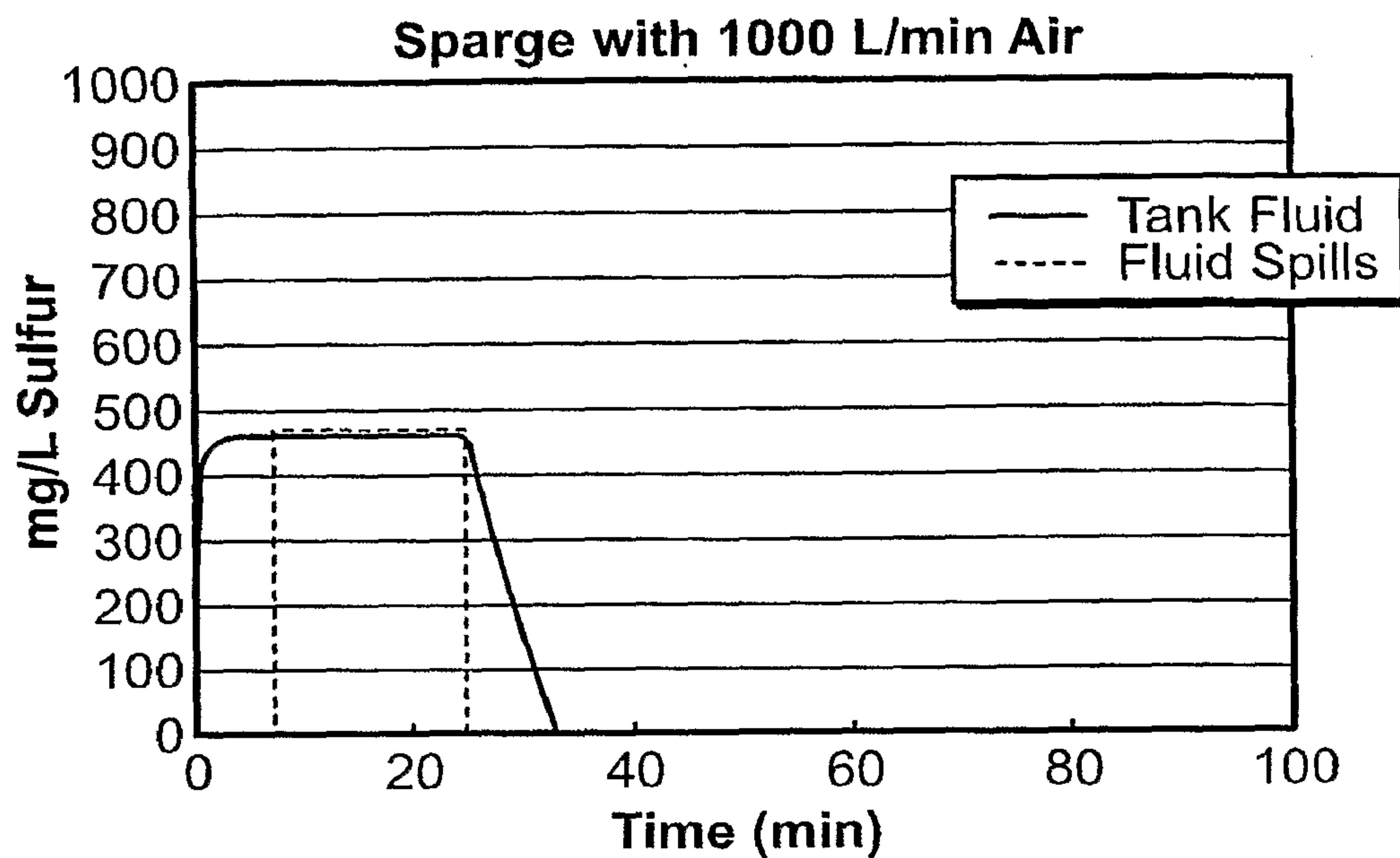
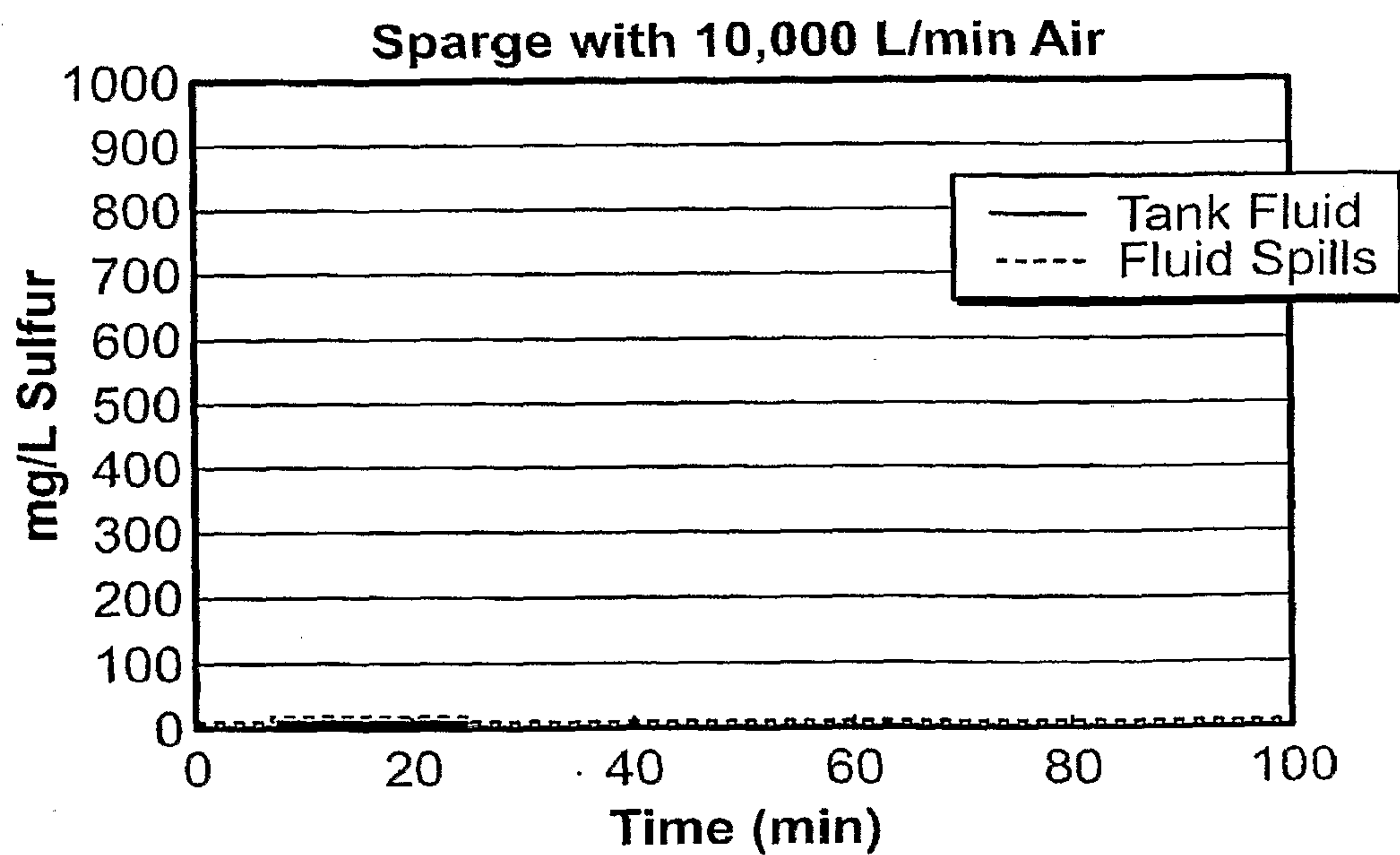
6/8

**FIG. 10****FIG. 11**

7/8

**FIG. 12****FIG. 13**

8/8

**FIG. 14****FIG. 15**

