

SUBMERGIBLE BIOCIDES REACTOR AND METHOD

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Patent Application Serial No. 62/152,342 filed on April 24, 2015, and U.S. Patent Application Serial No. 15/135,036 filed on April 21, 2016, the disclosures of which are incorporated herein by reference in their entireties.

BACKGROUND

[0002] Biocides can be used to control, reduce, and/or eliminate microbial growth that may occur on inner surfaces of industrial water systems. For example, inner surfaces of cooling water systems may become fouled with scale, which can provide a medium for microbial growth and lead to ineffective performance of the cooling water system. Control, reduction, and/or elimination of microbial growth can be important for efficient operation of industrial water systems.

SUMMARY

[0003] A method of administering biocide to industrial water in an industrial water process is provided. The method comprises diverting a portion of industrial water to a side stream at a water level. The industrial water side stream is filtered. A first reactant and a second reactant are added to a biocide-forming reactor at a ratio sufficient to form biocide. The biocide-forming reactor is located at least partially below the industrial water level. The filtered industrial water side stream is treated with biocide from the biocide-forming reactor. The biocide-treated industrial water side stream is returned to the industrial water in the industrial water process.

[0004] A reactor for generating an oxidative biocide and delivering the oxidative biocide to a liquid stream is provided. The reactor comprises a body, a reaction chamber, a first inlet port for receiving a first biocide reactant, a second inlet port for receiving a second biocide reactant, and an outlet port in fluid communication with the reaction chamber. Each of the inlet ports is in fluid communication with the reaction chamber. Packing is positioned within the reaction chamber to facilitate mixing of the first and second reactants.

[0004a] In one aspect, there is provided a reactor for generating an oxidative biocide and delivering the oxidative biocide to a liquid stream, the reactor comprising:

a body comprising a reaction chamber, a first inlet port for receiving a first biocide reactant, a second inlet port for receiving a second biocide reactant, each of the inlet ports in fluid communication with the reaction chamber, and an outlet port in fluid communication with the reaction chamber; and

packing formed by a plurality of packing members and positioned within the reaction chamber to facilitate mixing of the first and second reactants,

wherein the reaction chamber defines a first diameter and each packing member defines a second diameter, the ratio of the first diameter to the second diameter being from

5 about 3:1 to about 8:1.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0005] FIG. 1 illustrates an embodiment of a reactor;

[0006] FIG. 2 illustrates an alternate embodiment of a reactor; and

[0007] FIG. 3 illustrates a flow chart of a system that can be utilized to carry out the
5 methods disclosed herein.

DETAILED DESCRIPTION

[0008] Reactors for generating an oxidative biocide and delivering the oxidative biocide to a liquid stream are provided. In preferred embodiments, an inventive reactor as provided herein is utilized to perform one or more of the inventive methods, also provided
10 herein.

[0009] In each of the embodiments illustrated in FIGs. 1 and 2, reactor 10 comprises body 12. The body forms the primary structure of the reactor and forms reaction chamber 14. Each of first inlet port 16 for receiving a first biocide reactant and second inlet port 18 for receiving a second biocide reactant are in fluid communication with
15 reaction chamber 14. The inlet ports allow reactants to enter the reaction chamber. Reaction chamber 14 is in fluid communication with outlet port 20. When the reactor is placed into service, outlet port 20 is in fluid communication with a conduit being utilized to transport a filtered side stream of an industrial water process (*see, e.g.*, FIG. 3).

[0010] In preferred embodiments, the reaction chamber of the body of the reactor
20 comprises packing 22. A sample portion of packing 22 is shown in the figures. However, packing 22 may substantially fill reaction chamber 14, leaving essentially only void space in the reaction chamber. When present, the packing is positioned within the reaction chamber to facilitate mixing of the first and second reactants. The packing generally includes an amount of occupied space and an amount of void space. The term “void
25 space” is not intended to mean space devoid of matter. Typically, the void space will be occupied by fluid matter, *e.g.*, gaseous matter, reactants (*i.e.*, actives), and/or inert liquid(s). In a preferred embodiment, the packing occupies from about 25 percent to about 75 percent of the volume of the reaction chamber. Conversely, in the preferred
embodiment, the void space of the reaction chamber occupies from about 75 percent to
30 about 25 percent of the volume of the reaction chamber. In a further preferred
embodiment, the packing occupies from about 50 percent to about 75 percent of the

volume of the reaction chamber, and conversely, the void space of the reaction chamber occupies from about 50 percent to about 25 percent of the volume of the reaction chamber.

[0011] In certain embodiments, the packing of the reaction chamber is formed by a fixed packing insert. In some embodiments, the fixed packing insert is fixably attached to the body, which in certain embodiments is molded with the body as a single structure.

[0012] In a preferred embodiment, the packing of the reaction chamber is formed by a plurality of packing members 24. The packing members may comprise random packing. For example, the packing members may be selected from the group consisting of: glass balls, ceramic balls, Raschig rings, Berl saddles, and combinations thereof. In

embodiments that comprise a plurality of packing members, the reaction chamber is configured to prevent the packing members from leaving the reaction chamber. For example, in certain embodiments, the inlet ports and/or the outlet port may comprise one or more openings that are smaller in cross-sectional area than the cross-section of each packing member. Alternately or in combination, the reactor may be arranged so that any opening having a larger cross-sectional area faces upward, thereby allowing gravity to act on the packing members.

[0013] In certain embodiments, the reaction chamber defines a first diameter and each packing member defines a second diameter. In certain embodiments, the ratio of the first diameter to the second diameter is from about 3:1 to about 8:1. In a preferred embodiment, the ratio of the first diameter to the second diameter is from about 4:1 to about 6:1.

[0014] In certain embodiments, the body of the reactor is formed from a halogenated plastic. Examples of halogenated plastics include, but are not limited to, polyvinyl chloride ("PVC"), chlorinated polyvinyl chloride ("CPVC"), chlorinated polyethylene, chlorosulfonated polyethylene, polychloroprene, polyvinylidene fluoride ("PVDF"), fluorinated ethylene propylene ("FEP"), and combinations thereof.

[0015] In certain embodiments, each of the first inlet port and the second inlet port are in fluid communication with the reaction chamber via respective inlet channels 16a and 18a. For certain combinations of biocide reactants, it is preferred to keep the first and second biocide reactants separated until each has entered the reaction chamber. For the circumstance described, utilization of a reactor having inlet channels that are arranged to deliver each of the first reactant and the second reactant into the reaction chamber via separate streams may be desired, such as the embodiment shown in FIG. 1.

[0016] However, for certain other combinations of reactants, it is preferable to mix the reactants as soon as reasonably possible in the reactor. Thus, in certain embodiments, the inlet channels 16a and 18a are arranged to deliver the first reactant and the second reactant into the reaction chamber via single stream 30. The single-stream configuration allows for the reactants to begin mixing with each other prior to entering the reaction chamber, which is believed to facilitate more uniform mixing within the reaction chamber.

[0017] In certain embodiments, the body of the reactor can be made from one or more pipe fittings constructed of materials suitable for contacting the biocide, the industrial water side stream, and/or the reactants. In certain embodiments, the body of the reactor is constructed of, *e.g.*, a halogenated plastic (*e.g.*, chlorinated polyvinyl chloride (“CPVC”)) bushing equipped with a plug constructed of, *e.g.*, a halogenated plastic (*e.g.*, CPVC). Appropriate holes and connector adaptations should be made to accommodate any necessary connector fittings. In a preferred embodiment, the body is molded as a one-piece, two-piece, or three-piece, or n-piece structure. For the two-, three-, or n-piece structures, the body can be assembled using the two, three, or n pieces by a person of skill in the art without undue experimentation. Preferably, the reactor is assembled as shown in the figures provided. Preferably, the reactor is used to perform the methods disclosed herein.

[0018] Methods of administering biocide to industrial water in an industrial water process are also provided. Generally, the methods involve administering oxidative biocide to industrial water in an industrial water process.

[0019] The method comprises diverting a portion of industrial water to a side stream at a water level. FIG. 3 illustrates an embodiment of system 101 that can be utilized for carrying out the methods disclosed herein. In the embodiment of FIG. 3, side stream 111 generally flows at a flow rate that allows the industrial water process to filter an equal volume of water as contained in the industrial water process in a time period of about one day to about one hour. For example, an industrial water process that contains about 400 gallons may operate a side stream at a flow rate of from about 400 gallons per day to about 400 gallons per hour, or an industrial water process that contains about 40,000 gallons may operate a side stream at a flow rate of from about 40,000 gallons per day to about 40,000 gallons per hour.

[0020] As illustrated in FIG. 3, industrial water side stream 111 is delivered via pump 113 to filter 115. The filtration removes a quantity of solids, which may include

microorganisms, from the industrial water side stream, even in the absence of biocide in the industrial water side stream. The removal of solids from the industrial water side stream lessens the overall oxygen demand of the industrial water process, and particularly of the industrial water side stream, which reduces the amount of biocide necessary to provide adequate microbiological control as compared to a non-filtered industrial water side stream. As it relates to this disclosure, “adequate microbiological control” is used to describe, for example, a biocide treatment method where the number of microorganisms is reduced by orders of magnitude within a certain time period, or in the situation where microbiological counts are maintained less than 1,000 CFU/mL, which was done for each example listed herein. For example, a biocide treatment method that kills 99.9% of microorganisms (*e.g.*, colony-forming units, or “CFU”) within a 72-hour period (*i.e.*, 3-log kill) may be considered adequate microbiological control.

[0021] In certain embodiments, the filtering is carried out via at least one of a single-pass cyclone, a sieve, and a centrifugal action vortex separator. In certain embodiments, suspended solids having an average particle size of from about 1 micron to about 50 microns that are present in the industrial water side stream are removed via the filtering, including from about 1 micron to about 25 microns, or from about 1 micron to about 10 microns. In certain embodiments, the filtration is carried out via a multi-stage filtration unit.

[0022] The embodiment of FIG. 3 includes optional water meter/switch 117. A first reactant 200a and a second reactant 200b are added to a biocide-forming reactor 10 at a ratio sufficient to form biocide. The reactor is located at least partially below the industrial water level. It is important to conduct the reaction below the water level of the filtered industrial water side stream in order to cool the reactor. Many of the reactions that may occur inside the reaction chamber are exothermic reactions. Locating the reactor at least partially below the industrial water level allows the reactor, and subsequently the reaction, to be cooled by the industrial water, *e.g.*, the filtered industrial water side stream.

[0023] For example, in certain embodiments, sulfuric acid is reacted with sodium chlorite to form chlorine dioxide, which is an exothermic reaction. High temperature tends to degrade chlorine dioxide. Therefore, the cooling provided by the filtered industrial water side stream reduces the degradation and allows for better reaction efficiency.

[0024] In the embodiment of FIG. 3, filtered industrial water side stream 250 is treated with biocide from the biocide-forming reactor. In certain embodiments, the biocide

treating the filtered industrial water side stream provides a biocide concentration of from about 0.1 milligram to about 25 milligrams per liter of filtered industrial water. In a preferred embodiment, the biocide treating the filtered industrial water side stream provides a biocide concentration of from about 0.1 ppm to about 10 ppm, or from about 0.1 ppm to about 5 ppm.

[0025] In the embodiment of FIG. 3, biocide-treated industrial water side stream 300 is returned to the industrial water in the industrial water process. The filtration removes solid materials prior to addition of the biocide, which includes some microbial matter. Removal of solids from the industrial water, *e.g.*, the industrial water side stream, reduces the oxidant demand, which allows the biocide to persist at a higher residual concentration when returned to the industrial water process.

[0026] In certain embodiments, the first reactant is a halogen-containing salt. For purposes of this disclosure, examples of halogen-containing salts include, but are not limited to, chloride salts, fluoride salts, bromide salts, iodide salts, chlorite salts, and combinations thereof. The corresponding cation of the halogen-containing salt may be, for example, sodium, potassium, ammonium, and combinations thereof.

[0027] In certain embodiments, the second reactant is a chlorine-containing acid or salt thereof. For purposes of this disclosure, examples of chlorine-containing acids include, but are not limited to, hydrochloric acid and hypochlorous acid.

[0028] In certain embodiments, the first reactant is a chlorite salt and the second reactant is hydrochloric acid. The chlorite salt may be added as an aqueous solution at a concentration of from about 10 weight percent to about 40 weight percent. In a preferred embodiment, the chlorite salt is an alkali chlorite, *e.g.*, sodium chlorite, potassium chlorite, or combinations thereof. The hydrochloric acid may be added as an aqueous solution at a concentration of from about 10 weight percent to about 36 weight percent.

[0029] In certain embodiments, the first reactant is a fluoride salt and the second reactant is a hypochlorous acid or salt. The fluoride salt may be added as an aqueous solution at a concentration of from about 1 weight percent to about 4 weight percent. In a preferred embodiment, the fluoride salt is an alkali fluoride, *e.g.*, sodium fluoride, potassium fluoride, or combinations thereof. The hypochlorous acid may be added as an aqueous solution at a concentration of from about 5 weight percent to about 20 weight percent.

[0030] In certain embodiments, the first reactant is a bromide salt and the second reactant is a hypochlorous acid or salt. The bromide salt may be added as an aqueous solution at a concentration of from about 10 weight percent to about 90 weight percent. In a preferred embodiment, the bromide salt is an alkali bromide, *e.g.*, sodium bromide, potassium bromide, or combinations thereof. The hypochlorous acid may be added as an aqueous solution at a concentration of from about 5 weight percent to about 20 weight percent.

[0031] In certain embodiments, the first reactant is an iodide salt and the second reactant is a hypochlorous acid or salt. The iodide salt may be added as an aqueous solution at a concentration of from about 10 weight percent to about 30 weight percent. In a preferred embodiment, the iodide salt is an alkali iodide, *e.g.*, sodium iodide, potassium iodide, or combinations thereof. The hypochlorous acid may be added as an aqueous solution at a concentration of from about 5 weight percent to about 20 weight percent.

[0032] In certain embodiments, the first reactant is an ammonium salt and the second reactant is a hypochlorous acid or salt. The ammonium salt may be added as an aqueous solution at a concentration of from about 10 weight percent to about 30 weight percent. In a preferred embodiment, the ammonium salt is an ammonium halide and/or ammonium sulfate, *e.g.*, ammonium chloride, ammonium bromide, ammonium iodide, ammonium sulfate, or combinations thereof. The hypochlorous acid may be added as an aqueous solution at a concentration of from about 5 weight percent to about 20 weight percent.

[0033] In certain embodiments, the biocide comprises a reaction product selected from the group consisting of: chlorine dioxide, fluorine, chlorine, bromine, iodine, chloramine, and combinations thereof.

[0034] In certain embodiments, the method is performed such that the method has a flow-residence factor of from about 0.00001 to about 0.1, including from about 0.0001 to about 0.01, or to about 0.001. The flow-residence factor (FRF) is calculated by dividing the sum total volumetric flow rate of reactants (ΣRVF) by the volumetric flow rate of the industrial water side stream (SS), each having like units, and then multiplying the quotient by the total industrial water in the industrial water system (VOL), and dividing by the volumetric void space of the reaction chamber (VVS), in like units, leaving a unitless FRF. Formula 1 demonstrates calculation of the flow-residence factor.

$$FRF = (VVS / \Sigma RVF) * (SS / VOL)$$

Formula 1

In a preferred embodiment, the method has a flow-residence factor of from about 0.0001 to about 0.001.

[0035] The industrial water system may include a basin (*i.e.*, a sump), which may contain a relatively large amount of the industrial water of the industrial water system. In certain embodiments, the side stream is drawn from the basin. In certain embodiments, the side stream is returned to the basin. The industrial water system may include a condenser circulation line. For such embodiments, the side stream may be drawn from and/or returned to the condenser circulation line. In certain embodiments, side streams may be drawn from and/or returned to both the basin and the condenser circulation line.

[0036] For the Examples below, which are not to be limiting, the reaction chamber of the biocide-generating reactor had a diameter of 1.25 in. and a length of 1.5 in. The reaction chamber was filled with 6- to 8-mm glass balls that occupied 2/3 of the volume of the reaction chamber, leaving 1/3 of the reaction chamber volume as volumetric void space. The calculated void volume space for the reactor of the Examples is 0.6136 cubic inches, or 0.0026563 gallons.

EXAMPLE 1

[0037] A side stream is removed from and returned to a basin of an aqueous cooling system (an example of an industrial water system). The aqueous cooling system contains about 40,000 gallons of industrial water that is recirculated at 5,000 gallons per minute. The side stream is circulated at 60 gallons per minute, which will result in a turnover time of about 13 hours. The side stream is filtered using a multi-stage cylindrical filter comprising a coarse screen followed by a woven stainless steel wire mesh. The coarse screen includes 9 mm diameter holes, and the mesh includes passages of from about 5 to about 10 microns. After filtration, a resulting dose of 1.4 ppm chlorine dioxide is delivered to the side stream (*i.e.*, 1 lb/day of chlorine dioxide). In order to achieve the resulting dose, 0.67 gallons per day of 25 wt% aqueous sodium chlorite solution and 0.61 gallons per day of 32 wt% aqueous hydrochloric acid solution is delivered to the biocide-forming reactor, which is located at least partially below the industrial water level. The resulting FRF for this Example is approximately 0.00448, resulting in adequate microbiological control.

EXAMPLE 2

[0038] A side stream is removed from and returned to a basin of an aqueous cooling system (an example of an industrial water system). The aqueous cooling system contains about 40,000 gallons of industrial water that is recirculated at 5,000 gallons per minute.

5 The side stream is circulated at 60 gallons per minute, which will result in a turnover time of about 13 hours. The side stream is filtered using the filtration unit of Example 1. After filtration, a resulting dose of 4.2 ppm chlorine dioxide is delivered to the side stream (*i.e.*, 3 lb/day of chlorine dioxide). In order to achieve the resulting dose, 2.01 gallons per day of 25 wt% aqueous sodium chlorite solution and 1.83 gallons per day of 32 wt% aqueous
10 hydrochloric acid solution is delivered to the biocide-forming reactor, which is located at least partially below the industrial water level. The resulting FRF for this Example is approximately 0.00149, resulting in adequate microbiological control.

EXAMPLE 3

[0039] A side stream is removed from and returned to a basin of an aqueous cooling
15 system (an example of an industrial water system). The aqueous cooling system contains about 40,000 gallons of industrial water that is recirculated at 5,000 gallons per minute.

The side stream is circulated at 60 gallons per minute, which will result in a turnover time of about 13 hours. The side stream is filtered using the filtration unit of Examples 1 and 2. After filtration, a resulting dose of 1.4 ppm bromine is delivered to the side stream (*i.e.*,
20 1 lb/day of bromine). In order to achieve the resulting dose, 0.18 gallons per day of 42.8 wt% aqueous sodium bromide solution and 0.45 gallons per day of 12.5 wt% aqueous sodium hypochlorite solution is delivered to the biocide-forming reactor, which is located at least partially below the industrial water level. The resulting FRF for this Example is approximately 0.00911, resulting in adequate microbiological control.

EXAMPLE 4

[0040] A side stream is removed from and returned to a basin of an aqueous cooling
25 system (an example of an industrial water system). The aqueous cooling system contains about 40,000 gallons of industrial water that is recirculated at 5,000 gallons per minute.

The side stream is circulated at 60 gallons per minute, which will result in a turnover time
30 of about 13 hours. The side stream is filtered using the filtration unit of Examples 1–3. After filtration, a resulting dose of 1.4 ppm iodine is delivered to the side stream (*i.e.*,

1 lb/day of iodine). In order to achieve the resulting dose, 0.6 gallons per day of 20 wt% aqueous potassium iodide solution and 0.42 gallons per day of 12.5 wt% aqueous sodium hypochlorite solution is delivered to the biocide-forming reactor, which is located at least partially below the industrial water level. The resulting FRF for this Example is

5 approximately 0.00563, resulting in adequate microbiological control.

EXAMPLE 5

[0041] A side stream is removed from and returned to a basin of an aqueous cooling system (an example of an industrial water system). The aqueous cooling system contains about 40,000 gallons of industrial water that is recirculated at 5,000 gallons per minute.

10 The side stream is circulated at 60 gallons per minute, which will result in a turnover time of about 13 hours. The side stream is filtered using the filtration unit of Examples 1–4. After filtration, a resulting dose of 2.8 ppm chloramine is delivered to the side stream (*i.e.*, 2 lb/day of chloramine). In order to achieve the resulting dose, 1.55 gallons per day of 20 wt% aqueous ammonium sulfate solution and 2.79 gallons per day of 12.5 wt%

15 aqueous sodium hypochlorite solution is delivered to the biocide-forming reactor, which is located at least partially below the industrial water level. For this reaction, the aqueous sodium hypochlorite solution further comprised from about 1.5 to about 3 wt% sodium hydroxide, and the reaction product had a pH of from about 7 to about 9. The resulting FRF for this Example is approximately 0.00132, resulting in adequate microbiological

20 control.

[0042] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

25 [0043] The use of the terms “a” and “an” and “the” and “at least one” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of the term “at least one” followed by a list of one or more items (for example, “at least one of A and B”) is to

30 be construed to mean one item selected from the listed items (A or B) or any combination of two or more of the listed items (A and B), unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing”

are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0044] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

CLAIMS:

What is claimed is:

1. A reactor for generating an oxidative biocide and delivering the oxidative biocide to a liquid stream, the reactor comprising:

a body comprising a reaction chamber, a first inlet port for receiving a first biocide reactant, a second inlet port for receiving a second biocide reactant, each of the inlet ports in fluid communication with the reaction chamber, and an outlet port in fluid communication with the reaction chamber; and

packing formed by a plurality of packing members and positioned within the reaction chamber to facilitate mixing of the first and second reactants,

wherein the reaction chamber defines a first diameter and each packing member defines a second diameter, the ratio of the first diameter to the second diameter being from about 3:1 to about 8:1.

2. The reactor of claim 1, wherein the packing occupies from about 25 percent to about 75 percent of the volume of the reaction chamber.

3. The reactor of any one of claims 1 and 2, wherein the packing members are selected from the group consisting of: glass balls, ceramic balls, Raschig rings, Berl saddles, and combinations thereof.

4. The reactor of any one of claims 1 to 3, wherein the body is formed from a halogenated plastic.

5. The reactor of any one of claims 1 to 4, wherein the packing is formed by a fixed packing insert.

6. The reactor of claim 5, wherein the fixed packing insert is fixably attached to the body.

7. The reactor of any one of claims 1 to 6, wherein each of the first inlet port and the second inlet port are in fluid communication with the reaction chamber via respective inlet channels.

8. The reactor of claim 7, wherein the inlet channels are arranged to deliver each of the first reactant and the second reactant into the reaction chamber via separate streams.
9. The reactor of claim 7, wherein the inlet channels are arranged to deliver the first reactant and the second reactant into the reaction chamber via a single stream.
10. The reactor of claim 9, wherein the inlet channels merge at tapered angles to form the single stream.
11. The reactor of claim 10, wherein the tapered angles form a right angle at the single stream.
12. The reactor of claim 1, wherein the ratio of the first diameter to the second diameter is from about 4:1 to about 6:1.