

## FRAC FLOWBACK WATER TREATMENT & RECOVERY SYSTEM

### Marcellus Shale Deposit **Frac Water Make-up**

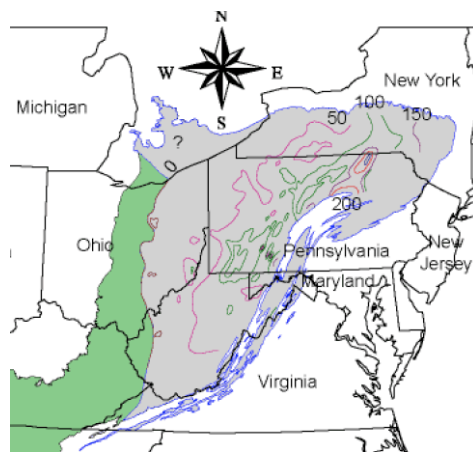
From 1 to 10 million gallons of fracture, “frac”, water, mixed with various additives, is required to completion fracture each horizontal deep well. Once used, this now contaminated water must be removed from the well, generally 10 to 40% is recovered, and is commonly referred to as “flowback” water. Typically, flowback water contains high dissolved solids with varying levels of various other constituents such as barium and strontium.

### Conditions

Due to the high dissolved solids content and presence of various other constituents, disposal of flowback water is becoming very difficult and costly.

Obtaining the needed water to makeup frac water, with subsequent disposal of the flowback water, presents a significant problem for gas production firms. In many areas, the amount of suitable water needed for formulation of frac water is just not available.

The best solution to this combined wastewater disposal and water supply problem is to simply treat and recycle the flowback water, over and over again, as frac water.



The Pennsylvania Department of Conservation and Natural Resources publishes a map that indicates which formations are likely to contain acid-forming minerals. The lower part of the Marcellus formation is on the map.

In many areas of the state where the Marcellus shale is present, the same conditions of acid mine drainage exist from past coal mining activities and the same metals are present in large amounts and is a major water quality problem.

## Frac Water Make-up and the PPC Treatment

### Metals and acid-producing minerals

Marcellus shales are known, in some regions, to contain acid-producing minerals such as pyrite and sulfides.

The PPC system treated similar items in acid mine drainage from past coal mining activities and the same metals are present in large amounts and is a major water quality problem.

### Iron-Fe

Iron and iron alloys (steels) are by far the most common metals and the most common ferromagnetic materials in everyday use. Fresh iron surfaces are lustrous and silvery-grey in color, but oxidise in air to form a red or brown coating of ferrous oxide or rust.

After being exposed to air and water, oxidation of metal sulfides (often pyrite, which is iron-sulfide) within the surrounding rock and overburden generates acidity.

At a pH of about 4, ferric ion forms ferric hydroxide with minimum solubility

~ pH = 8



We know with improved oxidation treatment of your AMD. The process oxidizes Frac Water very efficiently with no moving parts. This facilitates the conversion of ferrous iron into precipitating ferric iron very quickly. The same action that oxidizes the Frac as it passes through the Turbojett also mixes very efficiently any [reagent drawn](#) into the rear of the Turbojett increasing coverage and effectiveness and significantly decreasing chemical usage. The Turbojett® disintegrates liquid into smaller drops, resulting in an increased surface area. Increased surface area results in higher oxygen transfer rates and also greater reaction rates.

### Known Process Parameters

Salts:	Untreated	Treated
1 Total Dissolved Solids TDS	41,700	106
2 Chloride Cl	25,300	59
3 Sulfate SO4	81	0

### Metals:

- 4 Arsenic As
- 5 Barium Ba
- 6 Cadmium Cd
- 7 Chromium Cr
- 8 Cyanide CN
- 9 Fluoride F 0.
- 10 Lead Pb
- 11 Total Mercury Hg

## FRAC FLOWBACK WATER TREATMENT & RECOVERY SYSTEM

### Known Process Parameters (continued)

12 Nitrate NO<sub>3</sub> as N  
13 Selenium Se  
14 Silver Ag  
15 Uranium U  
16 Copper Cu  
17 Iron Fe  
18 Manganese Mn  
19 Zinc Zn  
20 Aluminum A  
21 Boron Ba  
22 Cobalt Co  
23 Molybdenum Mo  
24 Nickel Ni Calcium  
25. Magnesium  
26. Potassium  
27. Sodium  
28. TSS  
29. Strontium

### 30 BTEX:

31 Benzene  
32 Toluene  
33 Ethylbenzene  
34 Total Xylenes

### Metals

**Name:** Aluminum

**Symbol:** Al

Barium

Name: Barium

Symbol: Ba

### Properties

Barium is a metallic element, soft, and when pure is silvery white; it belongs to the alkaline earth group, chemically resembling calcium.

The metal oxidizes very easily and should be kept under petroleum or other suitable oxygen-free liquids to exclude air.

It is decomposed by water or alcohol. In water, the more toxic soluble barium salts are likely to be converted to insoluble salts which precipitate. Barium does not bind to most soils and may migrate to ground water. It has a low tendency to accumulate in aquatic life.

## FRAC FLOWBACK WATER TREATMENT & RECOVERY SYSTEM

Barium is a soft silvery metallic alkaline earth metal. It is never found in nature in its pure form due to its reactivity with air. Its oxide is historically known as baryta but it reacts with water and carbon dioxide and is not found as a mineral.

The most common naturally occurring minerals are the very insoluble barium sulfate, BaSO<sub>4</sub> (barite), and barium carbonate, BaCO<sub>3</sub> (witherite).

Barium sulfate is used for its heaviness, it is used as an insoluble heavy mud-like paste when drilling oil wells.

### Uses

The most important compounds are the peroxide, chloride, sulfate, carbonate, nitrate, and chlorate.

Lithopone, a pigment containing barium sulfate and zinc sulfide, has good covering power, and does not darken in the presence of sulfides.

Barite is extensively used as a weighing agent in oil well drilling fluids, and is used in making rubber.

The carbonate has been used as a rat poison, while the nitrate and chlorate give colors in pyrotechnics.

The impure sulfide phosphoresces after exposure to the light. All barium compounds that are water or acid soluble are poisonous.

### Calcium

[Name:](#) Calcium

[Symbol:](#) Ca

Chemically calcium is reactive and soft for a metal.

It is a silvery metallic element that must be extracted by electrolysis from a fused salt like calcium chloride. Once produced, it rapidly forms a grey-white oxide and nitride coating when exposed to air.

It is somewhat difficult to ignite, unlike magnesium, but when lit, the metal burns in air with a brilliant high-intensity red light.

Calcium metal reacts with water, evolving hydrogen gas at a rate rapid enough to be noticeable, but not fast enough at room temperature to generate much heat.

In powdered form, however, the reaction with water is extremely rapid, as the increased surface area of the powder accelerates the reaction with the water. Part of the slowness of the calcium-water reaction results from the metal being partly protected by insoluble white calcium hydroxide. In water solutions of acids where the salt is water soluble, calcium reacts vigorously.

Calcium, though it has a higher resistivity than copper or aluminium, weight for weight, allowing for its much lower density calcium is a rather better conductor than either.

## FRAC FLOWBACK WATER TREATMENT & RECOVERY SYSTEM

Calcium as the element is a grey silvery metal. The metal is rather hard. Calcium is an essential constituent of leaves, bones, teeth, and shells. Calcium is the fifth most abundant element in the earth's crust and makes up more than 3% of the crust. Calcium does not occur as the metal itself in nature and instead is found in various minerals including as limestone, gypsum and fluorite. Stalagmites and stalactites contain calcium carbonate ( $\text{CaCO}_3$ ). Calcium carbonate is the basis of the cement industry. Calcium is classified chemically as one of the alkaline earth elements (that is, in Group 2 of the periodic table. The metal is rather reactive. It readily forms a white coating of calcium nitride ( $\text{Ca}_3\text{N}_2$ ) in air. It reacts with water and the metal burns with a yellow-red flame, forming largely the nitride.

### Magnesium

[Name:](#) Magnesium

[Symbol:](#) Mg

Magnesium, an alkaline earth metal, is the ninth most abundant element in the universe by mass. Magnesium ion's high solubility in water helps ensure that it is the third most abundant element dissolved in seawater.

Elemental magnesium is a fairly strong, silvery-white, light-weight metal (two thirds the density of aluminium). It tarnishes slightly when exposed to air, although unlike the alkaline metals, storage in an oxygen-free environment is unnecessary because magnesium is protected by a thin layer of oxide which is fairly impermeable and hard to remove. Like its lower periodic table group neighbor calcium, magnesium reacts with water at room temperature, though it reacts much more slowly than calcium.

When it is submerged in water, hydrogen bubbles will almost unnoticeably begin to form on the surface of the metal, though if powdered it will react much more rapidly.

The reaction will occur faster with higher temperatures (see precautions).

Magnesium also reacts exothermically with most acids, such as hydrochloric acid (HCl). As with aluminum, zinc and many other metals, the reaction with hydrochloric acid produces the chloride of the metal and releases hydrogen gas.

### Manganese

[Name:](#) Manganese

[Symbol:](#) Mn

Manganese ions have various colors, depending on their oxidation state, and are used industrially as pigments. The permanganates of sodium, potassium and barium are powerful oxidisers.

The metal is gray-white, resembling iron, but is harder and very brittle. The metal is reactive chemically, and decomposes cold water slowly.

It is an important component of steel. It is not normally necessary to make manganese in the laboratory as it is available commercially. Nearly all manganese produced commercially is used in the steel industry as ferromanganese. This made by the reduction of iron oxide,  $\text{Fe}_2\text{O}_3$ , and

## FRAC FLOWBACK WATER TREATMENT & RECOVERY SYSTEM

manganese dioxide,  $MnO_2$ , in appropriate proportions with carbon (as coke) in a blast furnace. Pure manganese is available through the electrolysis of manganese sulphate,  $MnSO_4$ . Manganese is a gray-white metal, resembling iron.

It is a hard metal and is very brittle, fusible with difficulty, but easily oxidized. Manganese metal and its common ions are paramagnetic. While manganese metal does not form a permanent magnet, it does exhibit strong magnetic properties in the presence of an external magnetic field. The most common oxidation states of manganese are +2, +3, +4, +6 and +7, though oxidation states from +1 to +7 are observed.  $Mn^{2+}$  often competes with  $Mg^{2+}$  in biological systems, and manganese compounds where manganese is in oxidation state +7 are powerful oxidizing agents.

### Important compounds

Methylcyclopentadienyl manganese tricarbonyl is used as an additive in unleaded gasoline to boost octane rating and reduce engine knocking. The manganese in this unusual organometallic compound is in the +1 oxidation state.

The most stable oxidation state for manganese is +2, which has a pink to red color, and many manganese(II) compounds are known, such as manganese(II) sulfate ( $MnSO_4$ ) and manganese(II) chloride ( $MnCl_2$ ). This oxidation state is also seen in the mineral rhodochrosite, (manganese(II) carbonate). The +2 oxidation state is the state used in living organisms for essential functions; all of the other states are much more toxic.

The +3 oxidation state is known, in compounds such as manganese(III) acetate, but these are quite powerful oxidizing agents.

Manganese(IV) oxide (manganese dioxide,  $MnO_2$ ) is used as a reagent in organic chemistry for the oxidation of benzylic alcohols (i.e. adjacent to an aromatic ring).

Manganese dioxide has been used since antiquity to oxidatively neutralize the greenish tinge in glass caused by trace amounts of iron contamination.  $MnO_2$  is also used in the manufacture of oxygen and chlorine, and in drying black paints. In some preparations it is a brown pigment that can be used to make paint and is a constituent of natural umber.

## Strontium

Name: Strontium

Symbol: Sr

Strontium is an alkaline earth metal, strontium is a soft silver-white or yellowish metallic element that is highly reactive chemically. The metal turns yellow when exposed to air. It occurs naturally in the minerals celestine and strontianite.

### Forms

Strontium is found chiefly as celestite and strontianite. The metal can be prepared by electrolysis of the fused chloride mixed with potassium chloride, or is made by reducing strontium oxide with aluminum in a vacuum at a temperature at which strontium distills off. Reacts out in our process cavity.

## FRAC FLOWBACK WATER TREATMENT & RECOVERY SYSTEM

### Properties

Strontium is softer than calcium and decomposes in water more vigorously. It does not absorb nitrogen below 380°C. It should be kept under kerosene to prevent oxidation. Freshly cut strontium has a silvery appearance, but rapidly turns a yellowish color with the formation of the oxide. The finely divided metal ignites spontaneously in air. Volatile strontium salts impart a beautiful crimson color to flames, and these salts are used in pyrotechnics and in the production of flares.

### Uses

Due to its extreme reactivity with oxygen and water, this element occurs naturally only in compounds with other elements, as in the minerals strontianite and celestite.

Strontium is a grey/silvery metal that is softer than calcium and even more reactive in water, with which strontium reacts on contact to produce strontium hydroxide and hydrogen gas.

It burns in air to produce both strontium oxide and strontium nitride, but since it does not react with nitrogen below 380°C it will only form the oxide spontaneously at room temperature. It should be kept under kerosene to prevent oxidation; freshly exposed strontium metal rapidly turns a yellowish color with the formation of the oxide.

### Alkaline Earth Metals

The alkaline earth metals are a series of elements comprising Group IIA: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).

The alkaline earth metals are silver colored, soft metals, which react readily with halogens to form ionic salts, and with water, though not as rapidly as the alkali metals, to form strong alkaline (basic) hydroxides.

For example, sodium and potassium react with water at room temperature, magnesium reacts only with steam and calcium with hot water:  $Mg + 2 H_2O \rightarrow Mg(OH)_2 + H_2$

Beryllium is an exception: It does not react with water or steam, and its halides are covalent. All the alkaline earth metals have two electrons in their valence shell, so the energetically preferred state of achieving a filled electron shell is to lose two electrons to form doubly charged positive ions.

The alkaline earth metals are named after their oxides, the alkaline earths, whose old-fashioned names were beryllia, magnesia, lime, strontia and baryta. These oxides are basic (alkaline) when combined with water. "Earth" is an old term applied by early chemists to nonmetallic substances that are insoluble in water and resistant to heating--properties shared by these oxides. Typically, flowback water contains high dissolved solids with varying levels of various other constituents such as barium and strontium.

This water has suspended solids; aluminum, barium, calcium, iron, magnesium, manganese, and strontium must be removed to a level measured as a maximum total hardness of 2,500 mg/l as CaCO<sub>3</sub>.

Calcium carbonate is a chemical compound with the chemical formula CaCO<sub>3</sub>.

Calcium carbonate is the active ingredient in agricultural lime, and is usually the principal cause of hard water.