HELP HELP HELP HELP …If you can find the time.

The notice of Public Hearing below has significant meaning for the sixteen to One mine and all the gold mines in the Western United States. Before any gold mining occurred, the earth was formed mineral rich deposits. An associate element to gold is arsenic. While I have done a great deal of research and held numerous discussions with California's water staff about the regulations impacting our important industry, any adjustment in attitudes remains marginal. YOU CAN HELP!

Read the notice below and take special interest in the paragraph below "The designated parties for this hearing are as follows:". Please apply to become a designated party. Many businesses are closing or driven from California. The world knows California has the most egregious unfriendly arbitrary, unnecessary, unreasonable and at times unlawful regulations in the United States.

The major work of preparing a permit falls on the shoulders of the water staff. The heavy players in perpetuating the injustices that have occurred to the sixteen to One mine and many others both in the mining business and non-mining businesses is well documented. The heavy hand of what…Fear? Cowards? Bully? Greed? Stupidity? Jealousy? Ignorance? Disinterest? Laziness? Rests with the politicians and their appointed Boards. The decision regarding the classification of ground water passing through our property will be given to the California Regional Water Quality Control Board Central Valley Region in February. The PUBLIC must send notice of participation by November 3, 2014 no later than 5pm in writing.

Instruction are in the Public Notice following this entry. I offer suggestions but recommend you read this topic for background of the issues. People unfamiliar with the Sixteen to One should have an interest in just what is taking place in California. It might be taking place in your state as well. I'm not saying that the regulators are evil, bad or any of the fear, greed etc. cited above. Maybe it is apathy or a lack of motivation to change and correct misguided behavior. You can contact me as well. I will be writing more this week on ideas. MMM

Concentrations of naturally occurring arsenic in ground water vary regionally due to a combination of climate and geology. Arsenic concentrations exceeding 10 µg/L appear to be more frequently observed in the western United States than in the eastern half. Arsenic release from iron oxide appears to be the most common cause of widespread arsenic concentrations exceeding 10 µg/L in ground water. This can occur in response to different geochemical conditions, including release of arsenic to ground water through reaction of iron oxide with either natural or anthropogenic (i.e., petroleum products) organic carbon. Iron oxide also can release arsenic to alkaline ground water, such as that found in some felsic volcanic rocks and alkaline aquifers of the western United States. Sulfide minerals are both a source and sink for arsenic.

(Discussions of arsenic in relation to human health, regulation of arsenic in drinking water, analytical and sampling methods, cycling in the environment and other issues can be found in a variety of publications. Some useful publications include <u>Abernathy et al. (1997)</u>, <u>Chappell et al. (1994)</u>, <u>Lederer and Fensterheim (1983)</u>, <u>National Academy of Sciences (1977)</u>, Nraigu (1994a, 1994b), and the World Health Organization (<u>1981</u>, <u>1986</u>, <u>1996</u>). Overviews of arsenic in the environment by <u>Cullen and Reimer (1989)</u> and Ferguson and Gavis (1972) also contain information pertinent to this discussion.)

Few analyses of ground water samples for methylated arsenic compounds are available compared with the number of inorganic arsenic determinations, suggesting that high arsenic in ground water associated with waste disposal is common. Sites associated with the production of inorganic arsenic pesticides locally have exceedingly high concentrations in ground water, although not all sites appear to have an anthropogenic source for the arsenic.

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Arsenic-Sulfide Mineral Relations

In oxic water, dissolution of sulfide minerals, most notably pyrite and arsenopyrite, contributes arsenic to ground and surface water in many parts of the United States. Arsenopyrite is the most common arsenic mineral (O'Neil 1995). Other common sulfide minerals can contain 1% or more arsenic as an impurity (e.g., pyrite, galena, sphalerite, marcasite, and chalcopyrite; Onishi 1978). Scorodite ($FeAsO_4.2H_2O$) can be stable in low-pH water with high arsenic/iron ratios (Langmuir et al. 1999), although breakdown to iron oxide can occur. Sulfide minerals are an important sink for arsenic in some sulfidic water.

Sulfide mineral oxidation has long been studied primarily because of concerns with the production of acid mine drainage that commonly contains toxic concentrations of inorganic

constituents. Pyrite is the most common gangue sulfide mineral associated with ore deposits, and therefore its effect on mine drainage is the most thoroughly studied. Because of the voluminous literature and the availability of recent summaries (Moses et al. 1987; Nicholson et al. 1988; Nicholson 1994; Rimstidt et al. 1994), the following discussion of pyrite oxidation is limited to a broad overview. Dissolution of arsenopyrite (FeAsS) recently has received increased attention because of environmental concerns and because of an interest in increasing recovery of gold from refractory sulfide ores.

Pyrite oxidation is a complex chemical process that may involve 15 or more steps resulting in an overall reaction commonly written as

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O ==> Fe(OH)_3 + 2\ H_2SO_4 \quad (1)$$

Because arsenic concentrations in pyrite generally range from about 0.02% to 0.5%, and may be as large as 6.5% (Kolker et al. 1998; also see page 16, National Academy of Sciences 1977), this reaction (Equation 1) can release a considerable amount of arsenic to the aqueous phase. The bacteria *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, and *Leptospirillum ferrooxidans* can increase reaction rates for sulfide mineral oxidation by about five orders of magnitude compared with abiotic reaction rates (Schrenk et al. 1998). *T. ferrooxidans* and *L. ferrooxidans* increase the oxidation rate indirectly by catalyzing the reaction between dissolved oxygen and Fe(II) to form Fe(III). The ferric iron can then oxidize pyrite, which is a much faster reaction than the reaction of pyrite directly by dissolved oxygen.

Bacterial oxidation of pyrite involving oxygen appears to occur only in water with a pH less than 4 (Arkesteyn 1980), except in water with high nitrate concentrations. Sulfide-mineral oxidation in circum-neutral ground water commonly is attributed to abiotic oxidation. Although abiotic oxidation is slow, because bacteria do not catalyze the reaction of dissolved oxygen with Fe(II) (Moses and Herman 1991), field studies clearly demonstrate pyrite oxidation in neutral and slightly alkaline ground water (Postma et al. 1991; Kinniburgh et al. 1994; Schreiber et al. 2000). Microbial examination of ground water in a zone with ongoing pyrite oxidation suggests that the oxidation is abiotic (Kinniburgh et al. 1994).

Aqueous nitrate in the presence of oxygen can oxidize pyrite at pH values > 5 (Appelo and Postma 1993). The overall reaction may be written as

$$10\ FeS_2 + 30\ NO_3^- + 20\ H_2O ==> 10\ Fe(OH)_3 + 15\ N_2 + 15\ SO_4^{2-} + 5\ H_2SO_4 \quad (2)$$
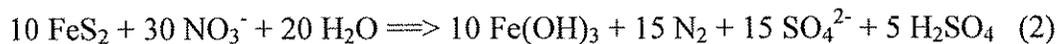
Bacterial oxidation of Fe(II) by *Gallionella ferruginea* and sulfur in pyrite by *T. denitrificans* promotes this reaction. Pyrite oxidation involving nitrate has produced arsenic concentrations well above 50 μg/L (van Beek et al. 1989; Appelo and Postma 1993).

Arsenopyrite oxidation by Fe(III) is about 10 times faster than the reaction with pyrite and is more rapid in the presence of *T. ferrooxidans*. Comparison of reaction rates is complicated by other factors, including surface area, degree of crystallinity, and mineral purity. As is the case for pyrite oxidation, *T. ferrooxidans* increases the reaction rate (Dorofeev et al. 1990; Fernandez et al. 1995; Zeman et al. 1995) by oxidizing Fe(II) to Fe(III). The overall reaction may be written as

$$FeAsS + 7/2 \ O_2 + 4 \ H_2O ==> Fe(OH)_3 + H_3AsO_4 + H_2SO_4 \quad (3)$$
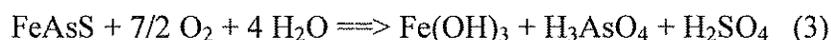
Arsenopyrite oxidation can lead to precipitation of scorodite under acidic conditions, but this product commonly breaks down to iron oxide (Dove and Rimstidt 1985; Alpers et al. 1994; Fernandez et al. 1995). For example, scorodite has been observed as an apparently stable alteration product of arsenic-rich sulfides in some mine dumps (Dove and Rimstidt 1985). Although the solubility of scorodite is somewhat uncertain (Dove and Rimstidt 1985; Robins 1987; Dove and Rimstidt 1987; Nordstrom and Parks 1987; Rimstidt and Dove 1987; Krause and Ettel 1988), it appears to be relatively soluble at intermediate pH values, and thus may not be an important control on arsenic in most ground water. Under higher pH conditions, iron oxide is the dominant oxidation product, and this reaction product adsorbs or co-precipitates arsenic.

Sulfide minerals, and perhaps amorphous sulfide phases, can be important sinks for arsenic in sulfidic water (Moore et al. 1988; McRae 1995; Rittle et al. 1995). The arsenic sulfide As_2S_3 can form abiotically or biotically from nonthermal water (Newman et al. 1997) and from geothermal water (Webster 1990). Arsenic adsorption or co-precipitation with iron mono-sulfide minerals, such as greigite or mackinawite, has been suggested to occur in shallow (< 10 cm), arsenic-contaminated sediments in two lakes; arsenic-containing pyrite forms beneath these sediments (Huerta-Diaz et al. 1998). Arsenopyrite, or a chemically equivalent amorphous phase (FeAsS), also can be a sink for arsenic (Rittle et al. 1995).

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Major arsenic minerals
Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. A list of some of the most common As minerals is given in Table 1.2. Most are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment. The greatest concentrations of these minerals occur in mineralised areas and are found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. The most abundant As ore mineral is arsenopyrite, FeAsS. It is generally accepted that arsenopyrite, together with the other dominant As-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth's crust. However, authigenic arsenopyrite has been reported in sediments by Rittle *et al.* (1995). Although often present in ore deposits, arsenopyrite is much less abundant than arsenian ('arsenic-rich') pyrite (Fe(S,As)$_2$) which isprobably the most important source of As in ore zones (Nordstrom, 2000).

Table 1.2 Major arsenic minerals occurring in nature
Mineral Composition Occurrence
Native arsenic As Hydrothermal veins
Niccolite NiAs Vein deposits and norites
Realgar AsS Vein deposits, often associated with orpiment, clays and
limestones, also deposits from hot springs
Orpiment As$_2$S$_3$ Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite CoAsS High-temperature deposits, metamorphic rocks

Arsenopyrite FeAsS The most abundant As mineral, dominantly mineral veins
Tennantite $(Cu,Fe)_{12}As_4S_{13}$ Hydrothermal veins
Enargite Cu_3AsS_4 Hydrothermal veins
Arsenolite As_2O_3 Secondary mineral formed by oxidation of arsenopyrite, native
arsenic and other As minerals
Claudetite As_2O_3 Secondary mineral formed by oxidation of realgar, arsenopyrite
and other As minerals
Scorodite $FeAsO_4.2H_2O$ Secondary mineral
Annabergite $(Ni,Co)_3(AsO_4)_2.8H_2O$ Secondary mineral
Hoernesite $Mg_3(AsO_4)_2.8H_2O$ Secondary mineral, smelter wastes
Haematolite $(Mn,Mg)_4Al(AsO_4)(OH)_8$
Conichalcite $CaCu(AsO_4)(OH)$ Secondary mineral
Pharmacosiderite $Fe_3(AsO_4)_2(OH)_3.5H_2O$ Oxidation product of arsenopyrite and other As minerals

Where arsenopyrite is present in sulphide ores associated with sediment-hosted gold deposits,
it tends to be the earliest-formed mineral, derived from hydrothermal solutions and formed at
temperatures typically of 100°C or more. This is followed by the formation of rarer native arsenic and
thereafter arsenian pyrite. Realgar and orpiment generally form later still. This paragenetic sequence
is often reflected by zonation within sulphide minerals, with arsenopyrite cores zoning out to arsenian
pyrite and realgar-orpiment rims. Oxides and sulphates are formed at the latest stages of ore
mineralisation (Arehart *et al.*, 1993).

Mineral-water interactions can be divided into two broad types from a geochemical point of view:
precipitation-dissolution reactions and *adsorption-desorption* reactions. *Precipitation-dissolution* reactions
involve the growth or erosion of a mineral structure and so only involve structural ions, i.e. those elements
included in the chemical formula of the mineral. The solubility of minerals can in principle be described quite
well by a solubility product, although this may vary with the particle size and crystallinity of the mineral. Also
the rate of dissolution or precipitation can be very slow and so thermodynamic equilibrium is often not attained
in practical time-scales.

The time taken to flush an aquifer depends on many factors (Appelo and Postma, 1994). A
critical factor is the number of pore volumes of 'fresh' water that have passed through the aquifer
since the initial release of arsenic has taken place. The greater the quantity of arsenic
involved, the more strongly it is adsorbed and the slower the rate of groundwater movement, the
longer that high-arsenic groundwaters will persist. It is clear that flat low-lying areas, particularly large
plains and delta regions, are particularly prone to potentially high arsenic groundwaters since they
combine many of the risk factors identified above. The process of delta development also favours the
separation of minerals based on particle size and produces the characteristic upwardly fining sequences of
sand–silt–clay which leads to confining or semi-confining layers which aid the development of strongly
reducing conditions.

Non-technical Summary
Arsenic in the environment
• Arsenic is a well-known poison. It has featured in history as a poison for killing people both
in fact and in fiction. It was once a popular poison because it conveniently left no easily
detectable trace. The analysis was difficult, and remains so.
• Arsenic is not that rare. Small amounts are found in all rocks, soils and sediments and arsenic
can be detected at low concentrations in most natural waters – rain, rivers, lakes, groundwater
and seawater. Occasionally it is present at much higher concentrations and this is of concern
where the water is being used for drinking water or irrigation. Groundwater presents a
particular risk since this is where most of the naturally high concentrations of arsenic have

been found and groundwater is often used as a source of drinking water.

The scale of the problem

● Well-known cases of arsenic poisoning from natural arsenic in the drinking water have been found in Taiwan, Chile, Argentina, Mexico, China and more recently in West Bengal (India) and Bangladesh. The scale of the problem in terms of population exposed to high arsenic concentrations is greatest in the Bengal Basin with perhaps 40 million people drinking water containing 'excessive' arsenic. Many of the worst problems occur in poor countries without the necessary infrastructure to be able to respond rapidly.

● The problem in Bangladesh was undetected for many years because of the lack of suitable arsenic testing laboratories within the country. The problem is made worse by the very large number of wells present. An estimate of 6–11 million wells has been made. Most of these are operated by hand-pumps and obtain their water from depths of 10–70 metres.

National drinking-water standards

● Each country defines the maximum amount of arsenic that it permits in drinking water. This is usually done formally through a national drinking-water standard. The WHO has set its provisional guideline value at 10 $\mu g\ l_{-1}$ but many countries have yet to adopt this standard in their legislation.

● The standard currently adhered to in India, Bangladesh and most of the countries which have groundwater arsenic problems is 50 $\mu g\ l_{-1}$ although the US-EPA and EC limits have both recently been reduced to 10 $\mu g\ l_{-1}$. The chronic or long-term toxicity of arsenic is believed to be such that if the standard basis for risk assessment that is applied to industrial chemicals were applied to arsenic, the maximum permissible concentration would be lower still.

The nature and causes of the problem

● The range of arsenic concentrations found in natural waters is unusually large, ranging from less than 0.5 $\mu g\ l_{-1}$ to more than 5000 $\mu g\ l_{-1}$, i.e. a range of greater than ten thousand times. Typical concentrations in freshwater are less than 10 $\mu g\ l_{-1}$ and often less than 1 $\mu g\ l_{-1}$. Rarely, much higher concentrations are found and this gives rise to arsenic problem areas. In such areas, the percentage of 'affected' wells (defined as those exceeding 50 $\mu g\ l_{-1}$) may exceed 10 percent of all wells and even in the worst cases, may exceed 90 percent of wells.

● These large-scale 'natural' arsenic groundwater problem areas are found all over the world but they tend to be confined to two types of environment: firstly, inland or closed basins in arid or semi-arid areas, and secondly, strongly reducing aquifers often derived from alluvium. Both types of susceptible environments tend to contain very young sediments and to be in low-lying, flat areas where groundwater flow is sluggish. Historically, these are poorly flushed aquifers and any arsenic released from the sediments has therefore been able to accumulate in the groundwater. Arsenic-contaminated groundwaters are also found in geothermal areas and, on a more localised scale, in areas of mining activity or where sulphide oxidation has occurred. There are likely to be other known problems in mining areas related to acid mine drainage (AMD) and the generally metal-rich waters. In most cases, these mineralized sources do not pose a major threat to drinking water supplies.

● Similarly, sources of geothermal water are usually well known and suitably monitored.

● Although the way in which the high-arsenic groundwaters are formed is not well understood in detail, some general features are emerging. These are listed below:

o the arsenic content of the aquifer materials does not appear to be exceptionally high – it is normally in the range 2–10 $mg\ kg_{-1}$;

o there appear to be two distinct 'triggers' that can lead to the release of arsenic from the aquifer material into the pore water. The first is the development of high pH (>8.5) conditions in semi-arid or arid environments usually as a result of the combined effects of mineral weathering and high evaporation rates. This pH change leads to the desorption of adsorbed arsenic (especially arsenate species) from natural mineral oxides, or prevents arsenic from being adsorbed in the first place. The second

trigger is the development of strongly reducing conditions at near neutral pH values, leading to the reductive desorption of arsenic from natural mineral oxides and to the reductive dissolution of iron and manganese oxides also leading to arsenic release. These are both responses to a change in the geochemical environment;

o there is as yet little direct evidence to support these arsenic release mechanisms for aquifers but the circumstantial evidence is strong. Detailed observations from other related environments such as lake and ocean sediments and soils, and from laboratory experiments with pure minerals, also lends credence to them;

o high concentrations of phosphate, bicarbonate, silicate and possibly organic matter, either individually or in combination, can enhance the mobility of arsenic in water through competition for adsorption sites;

o there is also potential for release of arsenic into groundwaters through the oxidation of sulphide minerals, particularly pyrite, brought about by aeration of the aquifer, for example by 'over-abstraction' of groundwater. However, compared with the 'ironoxide reduction hypothesis', the 'pyrite oxidation hypothesis' is not an efficient mechanism for releasing arsenic because of the readsorption of As by the iron(III) oxides that invariably precipitates further along the flow path.

The future

• Very little is known about how long it will take to flush out the arsenic released by the processes described above in specific aquifers. This is likely to depend on the past, present and future groundwater flows, and hence on the detailed palaeohydrogeology of the aquifer, and on the sediment chemistry. It is almost certainly longer than the timescales of relevance to the present groundwater As problems;

• the extent of flushing of an aquifer since the original deposition of the aquifer 'rocks' is clearly critical — the greater this is, the less likely it is that there will be an arsenic problem. This means that deeper, older aquifers will tend to suffer fewer problems (all other things being equal). Groundwater flows were greater than at present during the last glacial period (21,000–7,000 years ago) when sea levels were much lower and so aquifers laid down before this are less likely to be severely affected;

while we suspect that the arsenic problem will gradually disappear under natural groundwater flow, this may take many thousands of years and in the meantime, some wells may increase in arsenic concentration and some may decrease. Some of the arsenic may return via baseflow to be readsorbed by iron(III) oxides in the river sediments. The quantities of arsenic involved in affected aquifers are very large and there is little possibility of completely flushing it out in the short-term by pumping;

• a characteristic feature of high groundwater arsenic areas is the large degree of spatial variability – the well-to-well variability is usually large which means that it may be difficult to predict what the concentration of arsenic is likely to be in a particular well from the results of neighbouring wells. This means that in affected areas there is little alternative but to analyse each well separately for arsenic. Affected aquifers are the exception rather than the rule. In most aquifers, the majority of wells are likely to be unaffected even when they contain high concentrations of dissolved iron.

Acknowledgments

Source and behaviour of arsenic in natural waters

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