The Removal of Hexavalent Chromium From Drinking Water Supplies / Ground Water Remediation Sites And Industrial Wastewater

OCCURRENCE AND USES

Chromium, Atomic Number 24, Atomic Weight 51.996 is a metallic element in Group VIb of the Periodic Table of the Elements. The name "chromium" is derived from the Greek for "Color" probably because many salts of chromium are highly colored. Chromium naturally occurs in rocks, animals, plants, soil and in volcanic dust and gases. In its metallic state, chromium is stable and self-passivating, and is used as an ingredient in specialty alloys and steels, imparting superior corrosion resistance to the alloys. This is illustrated by the discovery that the "Terracotta Army" in Xian, China (Qin Dynasty, 3rd century BC) carried chromium-coated bronze lances and swords which, even after all these centuries exhibit no corrosive attack.

Chromium salts come in several different forms including trivalent chromium and hexavalent chromium. Trivalent chromium, often referred to as Chromium (III), or Cr^{+3}, is an essential, non-toxic, poorly absorbed nutrient for the human body. Deficiency of Cr^{+3} is reported to cause glucose intolerance. The safe and adequate daily intake of Cr^{+3} is stated to be 0.05 to 0.2 milligrams.

Hexavalent chromium, Chromium (VI), or Cr^{+6}, is generally used or produced in industrial processes. Water sources can be affected by hexavalent chromium naturally, or through contamination plumes from industrial centers, landfills and improper discharge of industrial processing streams.

EXPOSURE AND HEALTH EFFECTS

As stated, trivalent chromium is an essential micronutrient, whereas hexavalent chromium has been shown to be toxic, causing liver and kidney damage, internal hemorrhages and respiratory disorders. If inhaled, Cr^{+6} is known to cause cancer. On that basis, EPA classified it as a human carcinogen. The health effects of hexavalent chromium through ingestion (the dominant exposure route for drinking water) have seen only limited study which yielded uncertain conclusions. However, a study conducted by the National Toxicology Program (NTP) that was published in 2007 concluded that hexavalent chromium is carcinogenic when ingested in drinking water.

REGULATORY BACKGROUND

EPA

EPA currently regulates chromium Cr(VI), or Cr^{+6}, as part of the total chromium drinking water standard. EPA has an enforceable drinking water standard of 0.1 milligrams per liter (mg / L) or 100 micrograms per liter (µg / L) for total chromium, which includes chromium (VI) and chromium (III).

New health effects information has become available since the original standard was set, and EPA is reviewing this information to determine whether there are new health risks that need to be addressed. Additional information can be found on the chromium in drinking water website.

CALIFORNIA

In 1977 California Department of Health Services (CDHS) adopted what was then a "National Drinking Water Standard" for total chromium of 0.050 milligrams per liter (mg / L) or 50 micrograms per liter (µg / L). The total chromium MCL was established to address exposure to chromium (VI) the more toxic form of chromium. Chromium (III), (trivalent chromium) is a required nutrient.

Effective July 1, 2014 California Department of Public Health (CDPH) set the maximum contaminant level for hexavalent chromium (VI) at 0.010 milligrams per liter (mg / L) or 10 micrograms per liter (µg / L). Note: Refer to Drinking Water-Related Regulations at the Drinking Water Law Book.

HEXAVALANT CHROMIUM REMOVAL PROCESSES

- Reduction / Coagulation / Filtration (RCF)
- Anion Exchange
- Reverse Osmosis
- Electrodialysis (ED) and Electrodialysis Reversal (EDR)
- Coagulation Assisted Membrane Process (CAMP)
- Activated Carbon Filtration
- Lime Softening
- Titanium Dioxide Adsorption Enhanced By UV Light

Although some removal methods apply equally to trivalent as well as hexavalent chromium, the required treated water quality determines the selection of the removal process best suited for a particular application.

REDUCTION / COAGULATION / FILTRATION (RCF)

The Reduction / Coagulation / Filtration (RCF) process removes Hexavalent Chromium [Cr(VI)] from groundwater as follows: Ferrous sulfate ($FeSO_4$) is fed ahead of a reduction / contact vessel* to reduce hexavalent chromium [Cr(VI)] to trivalent chromium [Cr(lll)]. The excess ferrous iron (Fe^{+2}) is oxidized to ferric iron (Fe^{+3}) by the addition of chlorine. The trivalent chromium will form a co-precipitate with the ferric iron or be adsorbed onto the ferric floc.

*NOTE: The reduction / contact time required to convert Cr(VI) to Cr(lll) is approximately 1 – 2 minutes. The optimum contact time will be confirmed during a field pilot study.

The trivalent chromium / iron floc is removed by a multi-media filter system which includes a permanent media that does not require regeneration. The filter media is backwashed periodically to remove the floc (residual solids). 99.9% of the backwash water is reclaimed by settling the trivalent chromium / iron floc and by pumping the supernatant back to the raw water influent line. The non-hazardous ferric iron / trivalent chromium residual solids are either discharged to a sanitary sewer*, or, (if a sewer connection is not available), to a residual solids dewatering system. The dewatered residual solids “cake” is hauled off-site for disposal, and the filtrate water from the residual solids dewatering unit is returned to the backwash water reclaim tank. The residual solids thickening / dewatering system provides a “zero discharge” hexavalent chromium treatment process.

*Sewer authority discharge permit limits in California vary from 5 mg / L to 10 mg / L of total chrome. Consult the local sewer authority for their total chrome discharge limit.

NOTE: Refer to the RCF Process Drawing on page 6.

ANION EXCHANGE

Anion exchange, using either strong base or weak base synthetic resins, is an ideal process for the removal of chromate Cr(VI). In applications where the resin is not regenerated, weak base resins are used in “once-through” processes until exhaustion. This “disposable” resin has a typical “life span” of 1 – 2 years. Strong base resins are used in applications where the resin can be regenerated on-site and the spent brine can be discharged to a sewer. If the spent brine cannot be discharged to a sewer the strong base resin is exchanged and the spent resin is regenerated off site.

Raw water quality parameters such as chromium Cr(VI) concentrations, pH, T.D.S. temperature, organics, iron, manganese, chlorides, sulfate, etc., and the number of hours per day that the well operates, will determine the life span, bed volume to exhaustion / regeneration or exchange, and, ultimately, the type of resin selected.

REVERSE OSMOSIS

This membrane process is primarily designed for the desalting of saline or brackish waters by the application of hydrostatic pressure. This overcomes osmotic pressure and drives the water to be treated through a semi-permeable membrane designed to allow passage of water, but not of dissolved contaminants. The process requires expensive and fragile membrane stacks, either cellulose-acetate or thin film composite. Cellulose-acetate membranes can be operated at up to 400 psi, but are subject to biological attack and hydrolysis. They also allow the salt passage to double after a service life of about 3 years.

The more expensive thin film composite membranes are capable of the same or greater flux rate, but at half the applied pressure. These allow only a less than 30% increase in salt passage after 3 years. Both require considerable pre-treatment to prevent scaling, plugging, and colloidal or biological fouling of the membranes. Since the recovery of product water, as a percentage of feed water, is a function of applied hydrostatic pressure (up to 400 psi or more), the process tends to be quite energy intensive.

Most reverse osmosis plants are designed for 75-80% recovery, i.e., up to 25% of the flow will require proper disposal as a concentrated, possibly hazardous, waste (Montgomery). Reverse osmosis is quite capable of the removal of chromium to very low levels. Process operation and maintenance costs, as well as labor intensity, may tend to rule out its application for all but small volume treatment systems.

ELECTRODIALYSIS (ED) AND ELECTRODIALYSIS REVERSAL (EDR)

ED is an electrochemical membrane process initially developed for the treatment of saline or brackish waters. Instead of hydrostatic pressure, the process uses an applied direct current (DC) voltage to move dissolved anions and cations from alternate cells through semi-permeable membranes. This purifies a portion of the feed water, while concentrating another. While capable of removing chromium to low levels, the process is equipment, energy and labor intensive. It also creates a concentrate which requires proper disposal, and is quite wasteful of water. EDR is an ED process which reverses the polarity of the electrodes on a controlled time cycle, which reverses the direction of ion movement in a membrane stack. Reversing polarity provides automatic flushing of scale forming minerals from the surface of the membrane. EDR typically requires little or no pretreatment to minimize fouling of the membrane. ED / EDR systems are not considered to be economically viable for any but very small installations.

COAGULATION ASSISTED MEMBRANE PROCESS (CAMP)

Coagulation assisted membrane process (CAMP) is considered to be a promising technology for pollutant removal because it can be applied over a wide range of water quality that contains high turbidity, iron, manganese, sulfate and nitrate. Low pressure membranes (e.g. microfiltration and ultrafiltration) are very effective in removing particulate chromium, but without a pre-coagulation step, low pressure membranes are ineffective at removing soluble chromium. Metal based coagulants, such as ferric chloride, can be used to bind the chromium which is then removed with the ferric floc on the membrane. The use of low pressure membranes eliminates the breakthrough of chromium-laden coagulant flocs (a typical occurrence with conventional granular media filters) by taking advantage of the membranes' particle barrier. Factors affecting the CAM processes include ferric chloride dosage, pH, mixing and floc formation (contact time). As with all membrane processes, provision for adequate pretreatment to control feed water quality should be taken to protect the membrane from fouling caused by particulate matter, scaling and biofouling to optimize membrane performance and life. Disposal of the reject coagulant (which is not considered to be a hazardous waste) can be to a sanitary sewer.

ACTIVATED CARBON FILTRATION

Activated carbon, either granular or powdered, is capable of effectively absorbing chromium in both the +3 and the +6 valence states. Activated carbon, of course, is non-selective for chromium only, thus will absorb many substances from the water. Once exhausted, the carbon will require replacement and disposal as a "hazardous waste", which may render this removal method excessively expensive.

LIME SOFTENING

Excess Lime Softening is the addition of a sufficiently high lime dosage, at times in excess of 1 gram per liter, to obtain a pH greater than 11.5. It has long been used for the removal of calcium and magnesium carbonate hardness, and is also capable of the removal of trivalent chromium that may be present, i.e., hexavalent chromium must first be reduced to the trivalent state. The addition of powdered activated carbon, though apparently not absolutely necessary, appears to enhance removal efficiency. While this is an old tried and true process, and while apparently quite capable of chromium removal, the process remains plant and chemical intensive, requires the recarbonation of the water, and produces large volumes of (potentially hazardous waste) sludge. For these reasons, unless there is also a demonstrated need for water softening, the process may not be deemed economically viable.

TITANIUM DIOXIDE ADSORPTION ENHANCED BY UV LIGHT

Adsorption of hexavalent chromium (Cr^{+6}) onto the inert catalyst Titanium Dioxide (TiO_2) is known to be generally ineffective. However, Photocatalysis (in this case TiO_2 activated in the presence of ultraviolet light) greatly enhances the capability to remove hexavalent chromium via two pathways. In the first pathway, Photocatalysis has the capability to quickly reduce hexavalent chromium (Cr^{+6}) to the trivalent (Cr^{+3}) form. Secondarily, the newly created trivalent chromium now has a strong affinity to adsorb onto TiO_2 while activated by the UV light.

The process of recapturing the TiO_2 catalyst requires the further use of a final ultrafiltration ceramic membrane barrier thus creating very high quality discharge. 100% of the TiO_2 catalyst is sent back to the front of the process to be reused while at the same time the process automatically backwashes the UF ceramic membrane.

The Photocatalytic process, including the TiO_2 recycling step, which removes Cr^{+3} from the TiO_2, is completely automated. The operating cost for this process is mostly in the form of electricity to power the UV lamps with additional cost associated with NSF approved chemical and the differential pressure across the ceramic membrane.

PILOT TESTING

Due to the fact that varying ground water quality can significantly affect the chromium removal processes, pilot testing at each job site is recommended. Raw water quality analyses should be made prior to pilot testing to determine all of the constituents in the water that can affect the chromium removal processes. The pilot treatment system should be designed to treat all of the constituents in the raw water that will affect the efficiency of the treatment process. On-site testing should be verified by raw and treated water samples that are tested by an independent certified laboratory.

The pilot process should include pretreatment equipment as dictated by the raw water quality analysis to assure continued treatment to below EPA standards and to maximize process runs and optimize resin /media / membrane / UV lamp life. The pilot system must verify removal of chromium throughout the process run cycle as well as determine pretreatment chemical requirements, and the following costs: operations, labor, media / resin disposal and replacement, membrane disposal and replacement, UV lamp power costs and replacement and / or regenerant brine disposal or resin exchange costs.

NOTES:

1. THE AUTOMATED PUREFLOW FILTRATION RCF CHROMIUM (VI) REMOVAL PROCESS OPERATES UNDER PRESSURE FROM THE WELL TO THE TREATED WATER STORAGE RESERVOIR AND / OR TRANSMISSION MAIN.

2. AN EXCESS OF FERROUS SULFATE IS FED AHEAD OF A REDUCTION / DETENTION TANK TO REDUCE Cr(VI) TO Cr(III) AND SODIUM HYPOCHLORITE IS FED TO OXIDIZE FERROUS IRON TO FERRIC IRON.

3. A PRESSURE VESSEL CONTAINING PERMANENT FILTER MEDIA, THAT DOES NOT REQUIRE REGENERATION, REMOVES THE FERRIC IRON / TRIVALENT CHROMIUM FLOC. THE FILTER MEDIA IS BACKWASHED PERIODICALLY TO REMOVE THE FLOC AND THE BACKWASH WATER IS SENT TO A RECLAIM TANK WHERE THE IRON / TRIVALENT CHROMIUM SOLIDS SETTLE TO THE BOTTOM OF OF THE RECLAIM TANK.

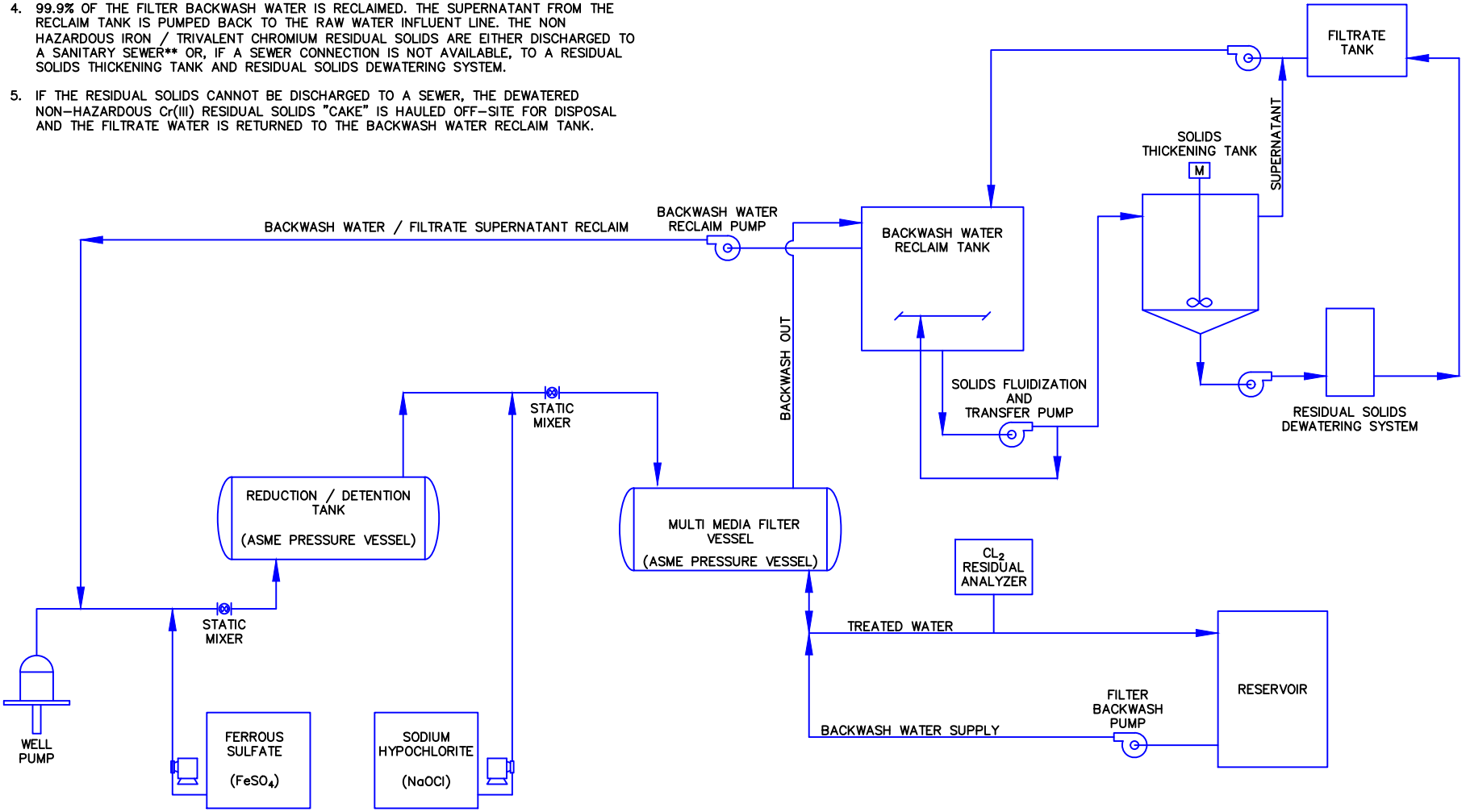
4. 99.9% OF THE FILTER BACKWASH WATER IS RECLAIMED. THE SUPERNATANT FROM THE RECLAIM TANK IS PUMPED BACK TO THE RAW WATER INFLUENT LINE. THE NON HAZARDOUS IRON / TRIVALENT CHROMIUM RESIDUAL SOLIDS ARE EITHER DISCHARGED TO A SANITARY SEWER** OR, IF A SEWER CONNECTION IS NOT AVAILABLE, TO A RESIDUAL SOLIDS THICKENING TANK AND RESIDUAL SOLIDS DEWATERING SYSTEM.

5. IF THE RESIDUAL SOLIDS CANNOT BE DISCHARGED TO A SEWER, THE DEWATERED NON-HAZARDOUS Cr(III) RESIDUAL SOLIDS "CAKE" IS HAULED OFF-SITE FOR DISPOSAL AND THE FILTRATE WATER IS RETURNED TO THE BACKWASH WATER RECLAIM TANK.

6. **THE RESIDUAL SOLIDS THICKENING / DEWATERING SYSTEM PROVIDES A "ZERO DISCHARGE" HEXAVALENT CHROMIUM TREATMENT PROCESS.**

7. **THE PUREFLOW RCF PROCESS WILL ALSO REMOVE ARSENIC, IRON AND MANGANESE FROM DRINKING WATER SUPPLIES.**

** SEWER AUTHORITY DISCHARGE PERMIT LIMITS IN CALIFORNIA VARY FROM 5 mg/L TO 10 mg/L OF TOTAL CHROME. CONSULT THE LOCAL SEWER AUTHORITY FOR THEIR TOTAL CHROME DISCHARGE LIMIT.



PROCESS	TITLE
REDUCTION/COAGULATION/FILTRATION (RCF) (ZERO DISCHARGE) CHROMIUM CR(VI) REMOVAL PROCESS	PUREFLOW FILTRATION DIV. PROCESS FLOW DIAGRAM WHITTIER, CA. (800) 926-3426

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Local Representative

PUREFLOW© FILTRATION SYSTEMS

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