



State Water Resources Control Board Division of Drinking Water

- TO: Carol Perkins Manager, Cal/EPA Scientific Peer Review Program Office of Research, Planning, and Performance
- FROM: Ashley Dummer, P.E. Senior Water Resource Control Engineer DIVISION OF DRINKING WATER
- CC: Melissa Hall, Division of Drinking Water Randy Barnard, Division of Drinking Water Robert Brownwood, Division of Drinking Water Kim Niemeyer, Office of Chief Counsel
- **DATE**: 10 August 2021
- **SUBJECT**: Request for External Scientific Peer Review of the Scientific Basis of Proposed Hexavalent Chromium Maximum Contaminant Level Best Available Technologies

# Best Available Technologies (BAT) for Hexavalent Chromium Treatment

This request is regarding developing a maximum contaminant level (MCL) for hexavalent chromium. The Division of Drinking Water requests that you initiate the process for external scientific peer review of the feasible technologies which may be considered best available technologies (BAT) for the treatment of hexavalent chromium, per the requirements of California Health and Safety Code (HSC) Section 57004.

## Purpose of Review

The primary purpose is to adopt an MCL for hexavalent chromium in drinking water, as required by HSC Section 116365. HSC Section 116365 requires that the State Water Board adopt MCLs as close to the public health goal (PHG) as is technologically and economically feasible at the time of the MCL adoption. The Office of Environmental Health Hazard Assessment (OEHHA) established a hexavalent chromium PHG of  $0.02 \mu g/l$  in drinking water in 2011.

Pursuant to HSC Section 116370, the State Water Board must adopt a BAT for any contaminant with a MCL at the time of the MCL adoption. Proposed regulations for a

E. JOAQUIN ESQUIVEL, CHAIR | EILEEN SOBECK, EXECUTIVE DIRECTOR

1001 I Street, Sacramento, CA 95814 | Mailing Address: P.O. Box 100, Sacramento, CA 95812-0100 | www.waterboards.ca.gov

hexavalent chromium MCL will include identified BAT for the treatment of hexavalent chromium to the proposed MCL concentration.

## When References will be Available at the FTP Site

#### 6 August 2021 Expected Date of State Water Board Hearing

Staff is scheduled to release the proposed regulations for publication in the California Regulatory Notice Register in December 2021 and present the proposed regulations to the State Water Board for adoption consideration in May 2022. To meet this schedule, we request receipt of the scientific peer reviews comments no later than 15 November 2021.

## Requested Review Period

We request that scientific peer review be accomplished within thirty (30) days of the review being initiated.

## Necessary Areas of Expertise for Reviewers

The Division of Drinking Water recommends a minimum of two reviewers. Each approved reviewer should be either an engineer or chemist and have expertise with hexavalent chromium removal in drinking water, including experience with the following treatment methods: ion exchange; reduction, coagulation, and filtration (RCF); stannous chloride; reverse osmosis (RO). Experience with multiple identified treatment methods is preferred. Each approved reviewer should be of sufficient technical expertise to review both conclusions found in Attachment 2. This requires the reviewer to (1) confirm the availability of means to estimate treatment costs for each technology designated as BAT, and (2) confirm the effectiveness, under full-scale field application, of each treatment method.

Refer to Attachment 2 for more details.

#### **Contact Information**

Ashley Dummer is the project manager: Ashley.Dummer@waterboards.ca.gov, (619) 525-4021.

#### Attachments

Attached please find:

- 1. Attachment 1: Plain English Summary.
- 2. Attachment 2: Scientific Assumptions, Findings, and Conclusions to Review.
- 3. Attachment 3: Individuals who Participated in the Development of the Proposal.
- 4. Attachment 4: References Cited.

# Attachment 1: Plain English Summary

The State Water Resources Control Board's (State Water Board) Division of Drinking Water is developing regulations to establish a maximum contaminant level (MCL) for hexavalent chromium in drinking water. Health and Safety Code (HSC) 116365 requires that the State Water Board establish the MCL as close to the public health goal (PHG) as is technologically and economically feasible. The hexavalent chromium PHG is  $0.02 \mu g/l$ . The hexavalent chromium MCL will be placed in the existing inorganic chemicals MCL table in the California Code of Regulations, Title 22, Section 64431-A. Hexavalent chromium will be regulated as an inorganic chemical in accordance with existing inorganic chemical regulations.

HSC Section 116370 further requires that at the time of MCL adoption, the State Water Board must adopt a finding of the best available technology (BAT). BAT is a treatment technology or technologies designated by the State Water Board as being capable of sufficiently treating drinking water for a given contaminant. The primary purpose of the BAT designation is assurance that a treatment technology exists to meet the proposed MCL. The BAT designation identifies the treatment technologies available at the time of MCL promulgation that can consistently and reliably remove the contaminant to a concentration at or below the proposed MCL.

To be identified as a BAT the treatment technology must be "effective under full-scale field application." "Effective" is taken to mean the technology has demonstrated that the technology can consistently and reliably produce treated water that complies with the proposed MCL, as water demand must be met 24 hours a day, seven days a week, 365 days a year. The technologies identified by the Division of Drinking Water have been piloted and studied to varying degrees in full-scale applications. To comply with HSC 116365 requirements to consider costs of compliance using best available technology, treatment technologies identified as BAT must also have cost data available.

Lack of a BAT designation does not preclude any appropriate technology from being used to meet an MCL. In many cases it simply means that when the MCL was promulgated, a technology had not yet demonstrated that it was effective under full-scale field application. Often a technology not designated as BAT must be studied further to demonstrate that it can be operated in a manner that produces treated water that meets the water quality objective or the proposed MCL. As with MCLs, BAT determinations may be reviewed and revised based on new information.

The State Water Board has evaluated the use of ion exchange, RCF (reduction, coagulation, and filtration), stannous chloride reduction, and reverse osmosis for hexavalent chromium in determining the economic and technological feasibility of a new MCL. Ion exchange, RCF, and reverse osmosis have been found to provide adequate treatment for hexavalent chromium in existing installations. Ion exchange, RCF, and reverse osmosis are the only BAT proposed at this time as other treatment techniques have not been identified and proven both effective and reliable.

The State Water Board's Division of Drinking Water proposes that the State Water Board find that ion exchange, RCF, and reverse osmosis are best available technologies for hexavalent chromium and add those technologies as BAT into California Code of Regulations, Title 22, Table 64447.2-A.

# Attachment 2: Scientific Assumptions, Findings, and Conclusions to Review

# Directions for Reviewers

The statutory mandate for external scientific peer review (California Health and Safety Code Section 57004) states that the reviewer's responsibility is to determine whether "the scientific portion of the proposed rule is based upon sound scientific knowledge, methods, and practices." Your task is to make this determination for the assumptions, findings, or conclusions below that the CalEPA External Scientific Peer Review Program has determined you can address with confidence, based on expertise and experience. (If you decide to address other assumptions, findings, or conclusions, identify the expertise and experience you are relying on to do so.) We also invite you to address these questions:

- Are there any scientific subjects that are part of the scientific basis of the proposal that are not described below?
- Taken as a whole, is the proposal based upon sound scientific knowledge, methods, and practices?

For further direction, please see the attachment, "Guidance for Reviewers," on the FTP site and sent to you with the letter initiating your review.

# Assumptions, Findings, and Conclusions

#### CONCLUSION

# 1. Ion exchange, RCF, and RO should be designated BAT for the treatment of hexavalent chromium.

The Division of Drinking Water has considered all available treatment technologies that are effective at treating hexavalent chromium to concentrations ranging from 1 to 30  $\mu$ g/L, have been proven under full-scale field applications, and have cost information available.

While RO has not been used to treat hexavalent chromium as a target contaminant at full scale, full scale applications have been shown to effectively remove incidental hexavalent chromium. In addition, RO is a mature technology that has shown to be a viable treatment for hexavalent chromium removal.

Ion exchange, RCF, and RO have been identified as being capable of reliably removing hexavalent chromium from drinking water to levels below 1  $\mu$ g/L, have been proven under full-scale field applications, and have cost information available; therefore, ion exchange and RCF meet the requirements to be designated as BAT.

Hazen and Sawyer (2013) estimated treatment costs for technologies for ion exchange and RCF. For each technology, the document also identified potential MCLs the

technologies could meet, typically ranging from 1 to 25  $\mu$ g/L. Treatment cost estimates for RO can be derived from RO performance on other contaminants.

#### a. Ion exchange

Hexavalent chromium in drinking water typically exists as chromate (CrO<sub>4</sub><sup>2-</sup>), an anion. Studies conducted with weak-base and strong-base anion (WBA and SBA, respectively) exchange resins have demonstrated the efficacy of using anion exchange technology to remove hexavalent chromium (Hazen and Sawyer, 2013; Seidel et al., 2014, Blute et al., 2015a; Parks et al., 2017). Using anion exchange technology in a lead-lag column configuration (in series) could result in a treated drinking water hexavalent chromium concentration of <1  $\mu$ g/L. The piloting work done by Hazen and Sawyer (2013) demonstrated that WBA exchange was capable of removing hexavalent chromium to below 1  $\mu$ g/L. Similarly, SBA exchange resins are also capable of producing water that would achieve an effluent hexavalent chromium concentration of 1  $\mu$ g/L (Seidel et al., 2014; Parks et al., 2017).

Based on the pilot work conducted to date, ion exchange technology should be considered for BAT designation. Aside from demonstrating the efficacy of the technology, the available reports contain specific treatment cost information.

### b. Reduction, coagulation, and filtration (RCF)

Gumerman et al. (1979) recognized that the combination of ferrous sulfate and filtration could be used to remove hexavalent chromium from drinking water. By using a reducing agent such as a ferrous salt or stannous chloride, hexavalent chromium is reduced to trivalent chromium. The form of trivalent chromium present in water has a very low solubility, which results in the formation of a precipitate that can be removed by filtration.

Hazen and Sawyer (2013) reported on pilot studies that demonstrated the efficacy of using ferrous salts and media filtration to remove hexavalent chromium from drinking water. The studies concluded that media filtration could achieve hexavalent chromium concentrations of <5  $\mu$ g/L. Blute et al. (2015a) provided revised treatment cost estimates for RCF using granular media and several membrane filtration systems as an alternative to media, covering the same flow range as Hazen and Sawyer (2013). Blute et al. (2015b) found that RCF using membranes could produce water with less than 1  $\mu$ g/L hexavalent chromium.

Blute et al. (2015b) notes that RCF is not appropriate for "very small" water systems, i.e., those serving less than 500 customers, which is part of their reason for not extending the RCF with media or membrane treatment cost estimates to below 100 gpm.

Chowdhury et al. (2016) used the cost equations from Seidel et al. (2013) to provide RCF treatment cost estimates to achieve a 5  $\mu$ g/L hexavalent chromium concentration in treated water.

Based on the numerous pilot studies and reports, RCF performance is well documented. However, unlike ion exchange technology that can achieve a <1  $\mu$ g/L hexavalent chromium concentration, RCF using granular media can only achieve <5  $\mu$ g/L. Only by switching to membrane filtration could the RCF treatment technology achieve <1  $\mu$ g/L hexavalent chromium.

#### c. Reverse osmosis (RO)

RO was evaluated by Brandhuber et al. (2004) as part of bench-scale evaluations for low-level hexavalent chromium removal. The authors concluded that, while RO was a mature technology capable of reducing hexavalent chromium to <2  $\mu$ g/L, the high loss of water precluded recommending the technology move forward to pilot testing (since the study was being conducted in a water-short area (southern California), the project advisory committee concurred with the recommendation). As a result, further study of RO to demonstrate the effectiveness of the technology to produce drinking water at fullscale was discontinued. Both Parks et al. (2017) and Seidel et al. (2013) noted that no full-scale RO systems could be located that were operating to remove hexavalent chromium.

A recent literature search was unable to locate any reports detailing full-scale RO hexavalent chromium removal performance in drinking water production that would meet the performance requirements of likely proposed hexavalent chromium MCL concentrations. However, two full-scale RO treatment plants in California (CA3610075 and CA3310083) used primarily for desalting show incidental treatment of hexavalent chromium from about 5 ug/L to <1 ug/L (SWRCB, 2021). There were many studies detailing the removal of hexavalent chromium from wastewaters, but none demonstrating removal to the concentrations under consideration for a proposed MCL.

Rad et al. (2009) did not include treatment cost estimates; however, treatment cost estimates can be derived from RO performance on other contaminants, such as arsenic. If the operating parameters are identical, then the treatment cost estimates for RO removal of one contaminant can be used for another contaminant.

However, given the current understanding of the principles behind RO technology, the State Water Board agrees with the conclusion in Brandhuber et al. (2004) that RO is a mature technology that should be considered as viable treatment for hexavalent chromium removal. Rad et al. (2009) also shows that under the right operational conditions, RO performance can be optimized to achieve the desired level of hexavalent chromium in the finished water.

# 2. Additional information is needed to designate Stannous Chloride a BAT for the treatment of hexavalent chromium.

For stannous chloride to be considered a BAT, additional information on the capability of the technology to meet the proposed MCL will be necessary, including information on reoxidation in the distribution system and the ability to meet a potential MCL without

exceeding the stannous chloride maximum use level (MUL). Additionally, information on cost and its effectiveness during full scale application is needed.

#### a. Stannous chloride (SnCl<sub>2</sub>) reduction

The first step of the stannous chloride treatment process is the same as the RCF process: removing hexavalent chromium by adding a reducing agent to convert hexavalent chromium to trivalent chromium. However, the trivalent chromium precipitate that is formed is not removed by filtration in the stannous chloride process, but instead remains in the finished drinking water distributed to the service population. Although the work by Brandhuber et al. (2004) was limited by a method detection limit of 4  $\mu$ g/L for hexavalent chromium, the study demonstrated that hexavalent chromium could be reduced by stannous chloride. However, they also observed reoxidation of trivalent chromium to hexavalent chromium by chlorine and chloramines, which could pose a health concern if the trivalent chromium is not removed prior to entering the distribution system.

Henrie et al. (2019) reported on work done at Coachella Valley Water District. The study selected a target dose of 0.5 mg-Sn/L based on bench-scale testing, which demonstrated the ability to consistently meet their water quality goal of 10  $\mu$ g/L hexavalent chromium (averaging around 8  $\mu$ g/L hexavalent chromium in the finished water). Bench-scale results from this work indicated that a higher dose of stannous chloride results in a lower hexavalent chromium finished water concentration. However, the actual time-weighted dosages of stannous chloride at the entry point ranged from 0.4 to 0.7 mg-Sn/L, which exceeds the MUL of 0.63 mg-Sn/L under the NSF/ANSI Standard 60.

The time-weighted average dose in this study exceeding the NSF Standard 60 MUL means that increasing the stannous dose is not permissible, raising two important issues. First, the use of stannous chloride might not be appropriate for situations in which the source water concentrations of hexavalent chromium exceeded those encountered in this study (13 to 21  $\mu$ g/L hexavalent chromium). Since the stannous chloride dosing studied by Henrie et al. (2019) exceeded the stoichiometric ratio by almost an order of magnitude, a higher source water hexavalent chromium concentration would require higher stannous chloride doses to achieve the desired finished water levels. Higher doses are not likely to be possible without exceeding the MUL. Second, the study reported average finished water hexavalent chromium concentrations in the 7-8  $\mu$ g/L range. If the MCL is set lower than this range, stannous chloride reduction alone will not be sufficient to meet the MCL. These limitations will need to be accounted for when the treatment technologies are evaluated for BAT designation once the proposed MCL is identified.

Henrie et al. (2019) also contains information indicating that the higher stannous chloride dose selected may be needed to reduce the reoxidation of trivalent chromium to hexavalent chromium by chlorine in the distribution system. While the chlorine residuals in the distribution system during the study were around 1 mg/L (a maximum of 4 mg/L is allowed), their work indicates higher stannous chloride doses are needed to

achieve lower rates of soluble trivalent chromium reoxidation to hexavalent chromium. Achieving optimal stannous chloride dosing to reduce hexavalent chromium to trivalent chromium and minimize reoxidation of trivalent chromium to hexavalent chromium appears to be possible, but the constraint imposed by the MUL may limit use. In addition, information is needed to understand how time in the distribution system impacts reoxidation to hexavalent chromium.

Henrie et al. (2019) did not include treatment cost estimates, which would be necessary to designate stannous chloride reduction as a BAT.

# Attachment 3: Individuals who have Participated in the Development of the Proposal

#### State Water Resources Control Board:

Mark Bartson, Division of Drinking Water Randy Barnard, Division of Drinking Water Neeva Benipal, Division of Drinking Water Robert Brownwood, Division of Drinking Water Ashley Dummer, Division of Drinking Water Melissa Hall, Division of Drinking Water Eugene Leung, Division of Drinking Water Bethany Robinson, Division of Drinking Water Sherly Rosilela, Division of Drinking Water Zachary Rounds, Division of Drinking Water Richard Sakaji, Division of Drinking Water Alison Sim, Division of Drinking Water Kim Niemeyer, Office of Chief Counsel

#### **Corona Environmental Consulting:**

Chad Seidel

WQTS, Inc.: Issam Najm

#### Hazen and Sawyer: Nicole Blute

# Attachment 4: References Cited

#### Introduction

All references will be provided at an FTP site or are accessible using the links below.

#### References

- Blute, N.; Wu, X.; Imamura, G.; Song, Y.; Porter, K.; Cron, C.; Fong, L.; Froelich, D.; Abueg, R; Henrie, T.; Ramesh, S.; Vallejo, F. (2015a) Assessment of Ion Exchange, Adsorptive Media, and RCF for Cr(VI) Removal. Water Research Foundation: Web Report #4423.
- Blute, N.; Wu, X.; Cron, C.; Fong, L.; Froelich, D.; Abueg, R. (2015b). *Microfiltration in the RCF Process for Hexavalent Chromium Removal from Drinking Water*. Water Research Foundation: Web Report #4365.
- Brandhuber, P., Frey, M., McGuire, M., Chao, P.F., Seidel, C. Amy, G., Yoon, J., McNeill, L., Banerjee, K. (2004). Low-Level Hexavalent Chromium Treatment Options: Bench-Scale Evaluation. Water Research Foundation: Web Report #2814.
- California State Water Resources Control Board (SWRCB) (2013). *Hexavalent Chromium MCL Initial Statement of Reasons DPH-11-005 August 4, 2013.* Retrieved from: <u>https://www.waterboards.ca.gov/drinking\_water/certlic/drinkingwater/documents/ HexavalentChromiumMCL/DPH-11-005HCMCLISOR.pdf.</u>
- Chowdhury, Z.; Bigley, S.; Gonzalez, W.; Porter, K.L.; Imamura, G.; Francis, C.; Blute, N.; Rhoades, J.; Westerhoff, P.; Bowen, A. (2016). *Compliance Planning and Evaluation of Technologies for Chromium (VI) Removal*. Water Research Foundation: Web Report #4445.
- Gumerman, R.C.; Culp, R.L.; Hansen, S.P. (1979). *Estimating Water Treatment Costs: Volume 1 Summary*. EPA-600/2-79-162a. Retrieved from: <u>https://nepis.epa.gov/Exe/ZyPDF.cgi/30000909.PDF?Dockey=30000909.PDF</u>.
- Hazen and Sawyer; Arcadis U.S./Malcolm Pirnie. (2013). *Hexavalent Chromium Removal Research Project Report to the California Department of Public Health.* Retrieved from: <u>https://www.glendaleca.gov/home/showdocument?id=14308</u>.
- Henrie, T.; Plummer, S.; Orta, J.; Bigley, S.; Gorman, C.; Seidel, C.; Shimabuku, K.; Liu, H. (2019). Full-scale demonstration testing of hexavalent chromium reduction via stannous chloride application. *AWWA Water Science*.

- Parks, J.L.; Mantha, A.; Edwards, M.; Kommineni, S.; Shim, Y.; Porter, K.; Imamura, G. (2017). Bench-Scale Evaluation of Alternative Cr(VI) Removal Options for Small Systems. Water Research Foundation: Web Report #4561.
- Rad, S.A.M.; Mirbagheri, S.A.; Mohammadi, T. (2009). Using Reverse Osmosis Membrane for Chromium Removal from Aqueous Solution. *World Academy of Science: Engineering and Technology 57*. Retrieved from: <u>https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.193.5725&rep=rep1&t</u> <u>ype=pdf</u>.
- Seidel, C.J.; Najm, I.N.; Blute, N.K.; Corwin, C.J.; Wu, X. (2013). National and California treatment costs to comply with potential hexavalent chromium MCLs. *Journal-AWWA*, 105.
- Seidel, C.; Gorman, C.; Ghosh, A.; Dufour, T.; Mead, C.; Henderson, J.; Li, X.; Darby, J.; Green, P.; McNeill, L.; Clifford, D. (2014). *Hexavalent Chromium Treatment with Strong Base Anion Exchange.* Water Research Foundation: Web Report #4488.
- SWRCB. (2021). Safe Drinking Water Information System and Water Quality Information Replacement databases. <u>https://sdwis.waterboards.ca.gov/PDWW/</u>