Geogenic and Anthropogenic Chromium Contamination in Groundwater in an Ophiolitic Area, Northeastern Iran

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Abstract Geology of Iran shows an ophiolitic belt around the central Iran micro-continent. One of the main ophiolite suites, with ca. 100km long and 15km wide, located northeastern Iran as Sabzevar ophiolite suite. Ultramafic rocks of this ophiolite suite, display a high concentration of chromium (1000-3000_{ppm}) as a compatible element, especially in pyroxene group minerals. Average Chromium content of this ophiolite suite in peridotites is 2558_{ppm}, with maximum 4525_{ppm} (in pyroxenite) and minimum 832_{ppm} (in dunite). Dunite layers lie underneath of these ultramafic rocks, containing chromite lenses (FeCr₂O₄) with 20.56wt% Cr₂O₃. Today, about 10 active mining sites excavate ultramafic rocks for chromite ore mineral and altered ultramafic rocks, serpentinite, dump as unconsolidated gangue materials along stream pathways. There is an unconfined aquifer just southern of this ophiolite range containing detrital altered ultramafic rocks with the high concentration of chromium minerals. In this study 23 groundwater samples, collected from unconfined serpentinite alluvium aquifer that shows cumulative increasing Cr towards south because of increasing residence time, and much more water-rock interactions. Total Cr concentrations in this aquifer are from 12 to 61µg/l, higher than normal level of Cr mentioned by WHO (2µg/l). On the other hand, discharging of chromite mine and mineral processing site, contaminate one of drinking well at Forumad village up to 61µg/l of total chromium.

Although trivalent Cr is an essential nutrient, in oxidation conditions with increasing Eh and pH, it changes to chromate (CrO₄⁻²) and dichromate (Cr₂O₇⁻²) as dissolved anions which will be toxic and carcinogenic in groundwater. Based on California EPA Office of Environmental Health Hazard Assessment (OEHHA), 7.2% of total Cr is hexavalent. Recent information indicates that hexavalent chromium varies from 50% to 90% of the total chromium in many water supplies.

Keywords Groundwater Contamination, Hexavalent Chromium, Serpentinite Aquifer, Chromite Mine, Sabzevar Ophiolite, Carcinogenic Chromium

1. Introduction

Serpentinities or altered ultramafic rocks are distributed around central Iran and always associated with ophiolite complexes. One of the biggest ophiolite suites located in north-eastern Iran called Sabzevar ophiolite, ca. 200km long and maximum 20km wide and 2100km² areas (Figure 1).

Figure 1. Sketch map of Sabzevar ophiolite suite (modified maps of Geology map of Sabzevar [1] and Geology map of Jajarm [2]) and its drainage systems, delineated by TauDEM [3], originated from highland ophiolite, discharged on two seasonal and temporary river basins located northern part and southern part of this ophiolite range, called Jovein River and Kale-Shur River respectively

Chromium in these ultramafic rocks exists as a trace element especially in pyroxene group minerals, olivine, and chlorite, and Cr as a major element exists in chromite, and spinel minerals. Chromite, ore mineral Cr, in this suite, represents more than 20% chromium [4]. Whole rock analyses of peridotite show Cr level from 832_{ppm} to 4525_{ppm} [4]. Alteration and weathering of these rocks generate serpentinite soil and sediments containing high-level Cr as alluvial fans in southern and northern plains of this highland. Drainage basins wash both sides of this ophiolite suite (Figure 1) and leach Cr into groundwater. On the other hand, water-rock interaction and oxidation conditions in aquifer dissolve Cr(III) into Cr(VI) (Figure 2). The pE-pH diagram describes the relative importance of Cr(III) and Cr(VI) at equilibrium and the dominant species (Figure 2). As a general rule, Cr(VI) is expected to predominate in highly oxygenated drinking water or when strong oxidants such as chlorine or even moderately strong oxidants like chloramine are added in water treatment plant. At low Cr concentrations in typical drinking water conditions Cr(VI) is present as monovalent HCrO_4^- below pH 6.5 and divalent CrO_4^{2-} between pH 6.5 to 10 [5, 6]. At very low or no oxygen levels, Cr(III) is the dominant species, which will be in cationic (Cr^{+3} , CrOH^{+2} , or Cr(OH)_2^+) or neutral (Cr(OH)_3) form depending on the pH [5,7]. Cr(III) tends to be extremely insoluble ($< 20 \mu\text{g/L}$) between pH 7 and pH 10, with minimum solubility at pH 8 of about $1 \mu\text{g/L}$ [5].

Maximum concentration level (MCL) of total Cr in drinking water regulated by Canadian Drinking Water Quality [8] National Primary Drinking Water Regulations (NPDWR) [9], and WHO [10], are $50 \mu\text{g/l}$, $100 \mu\text{g/l}$, and $50 \mu\text{g/l}$, respectively. Now a day because of the carcinogenic potential of hexavalent chromium, these regulations are subject to change.

Figure 2. Separation pE-pH diagram for aqueous chromium

The purpose of the present study is to find out total chromium level and Cr(VI) concentration in water resources of Davarzan area which is the important area because of proximity several active chromite mine, serpentinite and peridotite aquifers alluvium, large watershed basin, and populated area with several village and a big town, Davarzan (Figure 1).

2. Geological Setting

Geology of Iran shows an ophiolitic belt around the central Iran micro-continent. One of the main ophiolite

suite located north-eastern Iran called Sabzevar ophiolite suite. It has ca. 100km long and 15km wide containing ultramafic, gabbroic, diabasic and volcanic rocks and minor pelagic sediments such as chert and pelagic limestone. There are two large watershed basins with many sub-watershed basins located at the northern and southern part of Sabzevar ophiolite suite. This ophiolite suite with east-west trend shows high elevated mountains, more than 2000m high, and divides this area to two huge drainage basins at northern and southern mountain area (Figure 1). Ultramafic rocks contain the high concentration of chromium (1000-3000_{ppm}) [4], as a compatible element, especially in pyroxene group minerals. Average Chromium content of Sabzevar ophiolite suite in peridotites is 2558_{ppm} with maximum 4525_{ppm} in pyroxenite, and minimum 832_{ppm} in dunite, and 896_{ppm} in cumulates gabbro. Dunite rocks lay down at the base of harzburgite unit [4], with chromite (FeCr₂O₄) lenses that represent 20.56wt% Cr₂O₃. Since 1970, this chromitite horizon has been excavated by several active mines.

3. Materials and Methods

Based on EPA [11] procedure for analyzing drinking water, 1-liter plastic bottles were used for collecting water samples. These bottles were washed with detergent, rinsed with tap water, soaked 4 hours in 20%(V/V) nitric acid and finally rinsed with reagent water and dried with air. Electric conductivity (EC) and pH were measured on site by portable EC meter and pH meter. To remove micro-particles water samples filtered by 0.2 μ m filter

paper. To extend sample holding time for several weeks, pH of water samples reduced below 2 by HNO₃ and stored in the ice boxes. Total chromium concentration determined by atomic absorption spectrometry (AAS) at Shahrood Science and Technology Park. Cr(VI) converted from total chromium by factors of 0.5 and 0.9. Watersheds and flow networks were delineated by Terrain Analysis Using Digital Elevation Model, TAUDM, [3].

4. Findings

In this study 23 groundwater samples were collected from wells, springs and qanats, gently sloping underground channel with a series of vertical access shafts, mainly in serpentinite unconfined aquifer applied to drinking water and farming in Forumad watershed area including a town with ca. 50000 population and 10 villages with ca. 4000 population (Table 1). These water resources originate from upstream of the ultramafic mountain range, northern watershed, feeding serpentinite alluvial fan aquifer (Figure 3). These water resources are used for drinking and farming. Total Cr fluctuate between 11.66-60.61 μ g/l with mean of 27.72 μ g/l, (Figure 4, Figure 5) EC varies from 190 to 2420 μ S/cm with max frequency class 190-747 μ S/cm, (Figure 6) and pH changes from 6.5 to 7.5 (Figure 7). Cr vs. pH diagram indicates maximum Cr levels follow pH range of 6.5-7.5 (Figure 8). Collected sample from Forumad city center represents the highest total chromium level (60.61 μ g/l).

Table 1. Analyzed water samples from different water resources

Town/Village	Resource	Population	Host Rock	†Cr (μ g/l)	Mg (mg/l)	EC (μ S/cm)	pH	¥Cr(VI) (μ g/l)	‡Cr(VI) (μ g/l)
Abrud	Spring	2000	Ultramafic	11.66	23.79	370	6	5.83	10.49
Dehno	Qanat	200	Serpentinitic alluvium	13.99	68.83	1730	7	6.99	12.59
Pahnestan	spring	10	Ultramafic	15.15	53.58	440	7	7.58	13.64
Abrud	Qanat	2000	Ultramafic	15.15	53.93	740	6	7.58	13.64
Forumad	Tap water	5000	Serpentinitic alluvium	16.32	62.63	630	6.8	8.16	14.69
Ghelichi	spring	20	Ultramafic	16.32	61.96	780	6.8	8.16	14.69
Nahaldan	spring	1600	Serpentinitic alluvium	16.32	92.6	1470	6.5	8.16	14.69
Nahaldan	Qanat	1600	Serpentinitic alluvium	18.65	50	690	6	9.33	16.79
Mur	spring	100	Ultramafic	18.65	38.98	450	6.5	9.33	16.79
Aliabad_Bala	Qanat	120	Serpentinitic alluvium	19.81	47.21	410	6	9.91	17.83
Kahak	Qanat	400	Serpentinitic alluvium	20.98	24.29	1240	6.8	10.49	18.88
Aliabad_Bala	Stream	120	Ultramafic	20.98	43.15	330	6	10.49	18.88
Davarzan	Tap water	20000	Serpentinitic alluvium	23.31	39.02	480	6	11.66	20.98
Davarzan	well	20000	Serpentinitic alluvium	23.31	27.61	610	7	11.66	20.98
Forumad	Qanat	5000	Serpentinitic alluvium	27.97	29.74	450	6.8	13.99	25.17
Kelate_Sadat	spring	1500	Serpentinitic alluvium	30.3	23.87	800	6.5	15.15	27.27
Estarband	Qanat	1600	Serpentinitic alluvium	30.3	22.77	190	6.5	15.15	27.27
Bahman_Abad	well	200	Serpentinitic alluvium	39.63	67.27	2420	6.8	19.82	35.67
Forumad	well	5000	Serpentinitic alluvium	44.29	68.69	1250	6.5	22.15	39.86
Kahak	Qanat	400	Serpentinitic alluvium	48.95	33.92	1880	7.5	24.48	44.06
Suiz	Qanat	300	Serpentinitic alluvium	48.95	9.98	690	6.8	24.48	44.06
Forumad	well	5000	Serpentinitic alluvium	55.94	79.73	1350	7	27.97	50.35
Forumad	Tap water	5000	Serpentinitic alluvium	60.61	79.43	1240	6.5	30.31	54.55

†Cr is total Chromium, directly analyzed by AAS; ¥Cr(VI) and ‡Cr(VI) are calculated by factor 0.5 and 0.9 of total Chromium respectively

Figure 3. Digital Elevation Map (DEM) representing Forumad single watershed with catchments, and flow networks delineated by TAUDem[3], charging the unconfined Davarzan aquifer

Figure 4. Cr-EC diagram shows the relatively positive correlation between these two factors ($R^2 = 0.18$). Red, yellow, and green lines represent highest, mean, and median Cr concentration in water samples

Figure 5. Histogram of Cr shows high-frequency class is 11.66-21.45ppb

Figure 6. Electrical Conductivity histogram shows high-frequency class at 190-747.5 µS/cm

Figure 7. pH histogram shows high-frequency class at 6.5-7.

5. Discussions and Conclusions

High-level Chromium in ophiolitic rocks concentrated in mafic minerals such as olivine and pyroxene. Furthermore, spinel group minerals (e.g. Chromite) were genetically generated in ophiolitic rocks and mined for Cr demands. All active chromite districts are mined as open pit and their gangue plus ore minerals are dumped near the mine site especially along stream-net and natural drainage basin. In

the southern part of this area, there is a large watershed basin (Figure 3) which charge unconfined aquifers containing alluvial rock originated from northern ophiolitic rocks and chromite mines. Water-rock interaction in these aquifers geochemically influences on groundwater (Figure 9) which is pumped for drinking and farming demands. These Water resources are reserved into the unconfined aquifers with serpentinite and peridotite host rocks containing high-level Cr. Chromium concentration in these ultramafic rocks is ~1603_{ppm} in harzburgite, ~832_{ppm} in dunite, 3271_{ppm} to 4525_{ppm} in pyroxenite [4]. Chromite as the main Cr mineral contains 60wt% chromium. Chromium in mentioned rocks and associated minerals is trivalent. Water-rock interaction in theses oxid unconfined aquifers dissolve Cr bearing minerals and generate high concentration soluble chromium (Figure 2) (Table 1). Recent studies, however, have shown no harmful effects from low Cr(III) in the diet and there is no known biological mechanistic function for Cr(III) in cells calling into questions whether Cr(III) is truly an essential nutrient [13].

Figure 8. Cr-pH diagram shows fairly positive correlation, $R^2=0.13$

Figure 9. Raster map of distribution chromium concentration see text for details

In a given water sample, Cr(III) can be present in five forms (Figure 10): 1) as soluble Cr(III) species, 2) as a precipitated Cr(OH)_3 solid, 3) sorbed to the surface of Fe(OH)_3 and other oxides, 4) "fixed" inside oxides in a form that is relatively inaccessible from solution, and 5) complexed with natural organic matter (NOM) such as humic and fulvic acids [14]. Although Cr(VI) can undergo similar reactions, it is much more likely to remain soluble. If the iron hydroxide does not dissolve, the models predict that Cr(III) will be virtually 100% sorbed over the range from pH 6 to 11 (Figure 11).

Figure 10. Soluble Cr(III) in water, see text for explanation [10]

Figure 11. Model prediction of soluble Cr(III) and Cr(VI) in a drinking water sample in the presence of iron particles. Conditions: Cr(III) or Cr(VI) = 5 $\mu\text{g/L}$, Fe = 2 mg/L (4 mg/L Fe(OH)_3), I = 0.01 M, using diffuse layer model of Dzombak and Morel [15]

In contrast, Cr(VI) will be virtually 100% soluble above pH 8.0, while at pH 2-6 less than 10% of Cr(VI) is soluble (Figure 11). Sorption of Cr(VI) to iron oxides or hydroxides starts to become highly significant (> 50%) below about pH 7. Cr(VI) also forms no significant precipitates at levels encountered in potable water and does not strongly bind to natural organic matter. Hence, Cr(VI) is generally present in drinking water as a soluble anion, and its potential human toxicity is a much greater concern than Cr(III). Although we analyzed total chromium in these water resources, Cr(VI) is the main ion with increasing pH 6 to pH 8 (Figure 11). Based on Morry [12] hexavalent chromium is 50 to 90% of the total chromium in many water supplies.

Hexavalent chromium is classified as a known human

carcinogen by inhalation routes of exposure [16,17]. Because of the lack of data on carcinogenicity of hexavalent chromium to humans via oral routes of exposure from drinking water, National Toxicology Program [18] and Stout et al, [19] concluded that hexavalent chromium, as sodium dichromate dihydrate, in drinking water caused oral cancers in rats and cancer of the small intestine in mice. Ingestion of hexavalent chromium in drinking water by human changes hexavalent chromium to trivalent chromium with the formation of Cr-DNA adducts and other DNA damage resulting in mutagenesis, cell proliferation and tumor formation in the GI tract California [20, 21, 22, 23] (Figure 12).

Figure 12. Cancer effects in humans from ingestion of hexavalent chromium in drinking water [20, 21, 22, 23].

The World Health Organization (WHO) in 2003 [10] set the provisional guideline value for total chromium in drinking water at 50 µg/l. But this regulation was set prior to the publication of the NTP and other recent health effects studies. A non-enforceable Public Health Goal (PHG) for hexavalent chromium of 0.02 µg/l (20 ppt) was issued in July 2011 by California OEHHA [20], and California will now proceed with setting an MCL for hexavalent chromium.

Based on WHO [10] guideline for total chromium two water samples, 60.61 µg/l, 55.94 µg/l were more than 50 µg/l and another two samples with 48.95 µg/l were around to this guideline. Moreover, based on Public Health Goal for hexavalent chromium all samples were higher than 0.02 µg/l. So, in this area individuals should be medical check-up for cancer risk of gastrointestinal (GI) tissue and remediation of Cr(VI) in potable water must be considered.

5.1. Remediation

It is not clear how much of total chromium in the groundwater are Cr(III) or Cr(VI), but it is clear, and Cr(III) could be converted to Cr(VI) in oxidant aquifer and by added oxidants (such as potassium permanganate) and disinfectants (chlorine, chloramine) used in the treatment

plant. Some of the most common remediation strategies utilize oxidation-reduction reactions, converting Cr(VI) to Cr(III). Reducing Cr(VI) in water resource will be achieved by physical (ion exchange), chemical, and biological reduction processes. Among these processes, chemical remediation is a cost-effective and convenient plan for unconfined aquifers. Injection of an electron donor such as hydrogen sulfide (H₂S) [24], sodium dithionite (Na₂S₂O₄) [25], sodium metabisulfite (NaHSO₃), calcium metabisulfite (CaHSO₃), FeSO₄, calcium polysulfide (CaS₅) [26], Fe(II) [27], Fe(0) [28], or tin(II) chloride (SnCl₂). Field testing has shown that sodium dithionite (Na₂S₂O₄), injected into an unconfined aquifer, successfully reduces chromate [29,30]. Existing wells or trenches can be used for chemical delivery. A more precise method of delivering liquid chemicals to the subsurface uses high-pressure injection technology, also called jetting [31]. Monitoring indicated that the treatment zone remained anoxic after 2 years and that chromate remained undetected. Additionally, operation and maintenance costs are low and no pumping and aboveground treatment are required.

Acknowledgements

We would like to thank peoples who supported us logistically and assisted us in the field. The authors are grateful to anonymous reviewers for their suggestions and recommendations.

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