Geochemical study of chromium in the Aktobe region of Kazakhstan

BSc in Geology

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ABSTRACT

Chromium and its derivatives are extensively used worldwide in various industries, resulting in vast amounts of this metal being released into the environment. Chromium-VI is a well-known toxin and carcinogen generated by anthropogenic activities. Pollution with hexavalent chromium is a severe environmental concern in many countries, including Kazakhstan, since it is the first largest chromium manufacturer globally. In order to discharge the water bodies and soils contaminated with hexavalent chromium, it is essential to predict the physicochemical conditions prevalent in the aqueous environment and soil. If there is a prevalence of any waste and heavy metals, it is vital to treat the water prior to discharge. Several toxic chromium remediation strategies are being used worldwide; however, they have not been implemented in Kazakhstan yet. In this research, three methods of chromium reduction are proposed: chemical reduction, bacterial reduction, and ion exchange. A geochemical modeling study should make it possible to choose the accurate method for hexavalent chromium reduction.

ORIGINALITY STATEMENT

‘I hereby declare that this research thesis is the result of my own work and to the best of my knowledge it contains no materials previously published or written by another person, all sources of information including figures, tables, and other materials are explicitly acknowledged in the thesis.’

Alin Serikova

Signed: Alin Serikova

Date: 03/05/2022

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1 INTRODUCTION

1.1 Background

Kazakhstan is ranked first in chromite ore reserves, followed by South Africa and Turkey, whereas it holds second place in production. All chrome reserves are localized in the Western part of Kazakhstan, the Aktobe region (Koshim et al., 2015). Specifically, the ore deposits and facilities are located near the small mining town of Khromtau, which is 90 km away from Aktobe city. The chromite deposits of Khromtau are located in the Kempirsay massif, on the southern edge of the Ural mountain system, and the Donskoy chromite deposits occur in the main orefield. On figure 1 below, it is seen that chrome deposits surround all sides of the city. Hence the ecological state of the Khromtau and adjacent territories is considered unfavorable for the citizens.

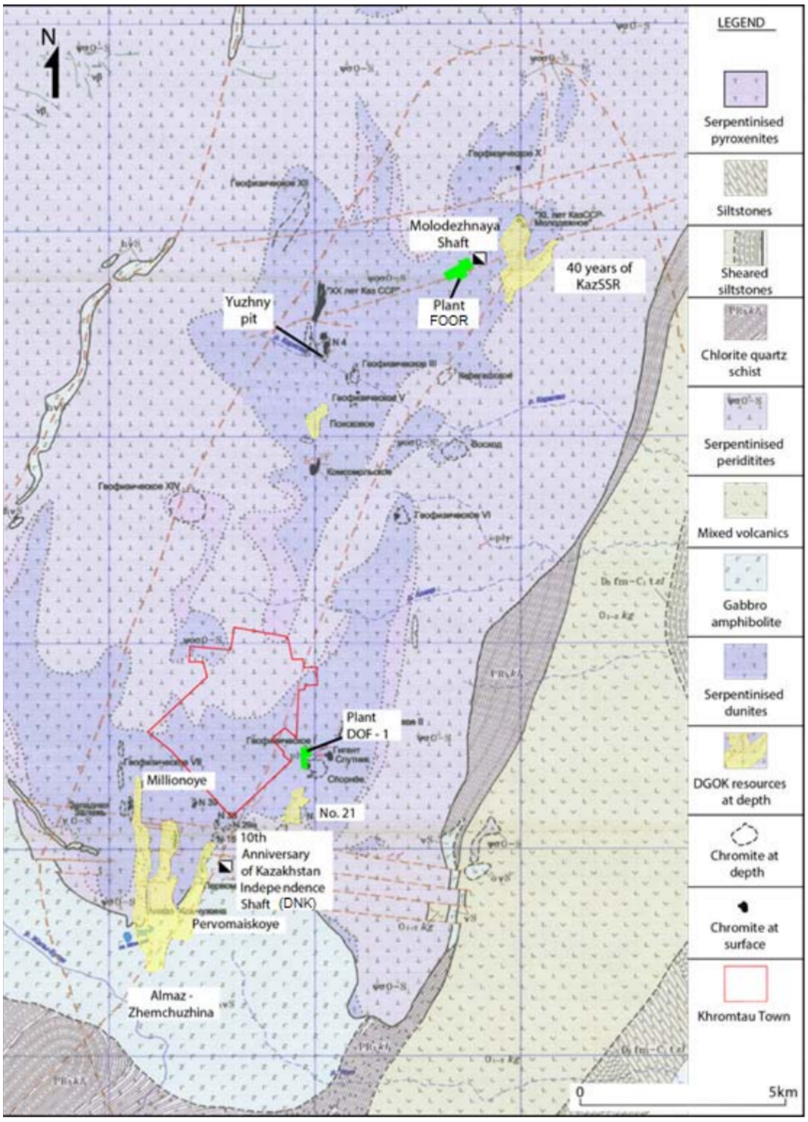

Figure 1 - Geological map of Khromtau (Kazchrome, 2017)

Several environmental problems involve the mining of chromium, one of them being that it pollutes the surrounding environment due to being a toxic, mutagenic, and carcinogenic metal. The chromium exists in two stable forms: Cr(VI) and Cr(III). Hexavalent chromium is a highly toxic and highly soluble metal. However, the trivalent one is less toxic and less soluble (Mishra and Sahu, 2013). In the mining environment, the waste is still high in chromium concentration. After that, industrial waste is used in landfills. Consequently, it disrupts the region's ecological balance and causes the leaching of hexavalent chromium from the soil into groundwater bodies, which contaminates water reservoirs. There are several landfills around Khromtau where the spoil from mining is stored in multiple tiers of more than 20 meters (Beketova et al., 2019).

The waste produced during mining includes slag, processed water, and dust that is very high in chromium concentration. Consequently, the air quality of the cities near the chromium mines is also poor, apart from water being polluted. The common possible routes of chromium exposure are inhalation, skin contact, and ingestion (Coetzee et al., 2020). These routes lead to tragic consequences such as lung cancer, skin burning, and gastrointestinal problems (Coetzee et al., 2020). As chromium belongs to the group of heavy metals, it tends to bioaccumulate. Bioaccumulation is defined as a rise in the concentration of a chemical element in a biological organism over time compared to its concentration in the environment. According to several research findings (Kudarov et al., 1989), the Khromtau region's land established a stable chromium biogeochemical province, resulting in an increase in chromium mobility in the biosphere: soil-plants-animal-people cycle. Chromium mining affects the environment in a negative way leaving the soil and water contaminated and toxic, which leads to poor health conditions for the population.

1.2 Problem statement

The dispersion of chromium in soils and groundwaters in the environment of the Aktobe region is of growing concern. The reduction of hexavalent chromium to trivalent chromium through bacteria, chemical agents, and synthetic resins has not been implemented in Kazakhstan yet. We propose here a review of geochemistry around serpentinites and peridotites, which host the chromium deposits of the Aktobe region, with the focus on developing measures to reduce the hexavalent chromium to trivalent chromium using chemical reduction, bacterial reduction, or ion exchange.

1.3 Project objectives

The general aim of the research thesis is to investigate the reduction of toxic Cr(VI) to non-toxic Cr(III) in the Aktobe region. The specific project objectives are:

- To construct some preliminary theoretical diagrams describing the stability relation of chromium in various environments and under different conditions;
- To investigate the potential methods of chemical and biological reduction of chromium as a remedial measure in cleaning up the impacted environment.

1.4 Scope of work

The study focuses on screening various approaches to toxic chromium reduction that can be applied in the environmental setting of Khromtau city. The initial work plan included a chromium mine site visit to collect water and soil samples. However, this was not possible due to mine site visit restrictions by Eurasian Resources Group (ERG), who is the owner of mines near Khromtau city. Hence, the study is limited to a review study and conceptual processes for the mitigation of adverse effects caused by hexavalent chromite.

1.5 Significance to the industry

The reduction of hexavalent chromium to trivalent chromium in groundwater of the Aktobe region is significant due to the threat chromium dispersion poses to the environment and population of that region. Although chromium remediation projects have not been conducted in Kazakhstan, chemical, physical, and biological chromium reduction methods might significantly improve the environmental conditions of the mine region. Establishing a qualitative model for the reduction of hexavalent chromium by various methods not only will help to address this issue but may also represent precious support for reserve estimation calculations.

2 LITERATURE REVIEW

2.1 Basics of Chromium

Chromium (Cr) is a metallic element initially discovered in the crocoite ($PbCrO_4$) mineral by Louis Nicolas Vauquelin. The mineral was extracted from the Ural Mountains in Russia (DeSarle, 2014). It is the 24th most abundant mineral in Earth's crust, whereas, in the mantle, it is the seventh prevalent element (Jagoutz et al., 1979).

More than 80 minerals containing chromium as a structural component have been identified, although the ones with economic value are Cr-rich spinels (up to 54 wt% Cr_2O_3). The metallic element chromium is mainly found within the chromite mineral, which has a chemical formula $FeCr_2O_3$ (Coetzee et al., 2020). The chromite ore is generated by the intrusion and solidification of molten lava. Alternative terminology used to describe chromite deposits includes chromitite, a cumulate rock composed of chromite minerals.

2.1.1 Sources of chromium in the environment

Chromium is found in the environment in various valence states, ranging from -2 to +6, the most stable of which is Cr(VI) and Cr(III), which have distinct features. Both hexavalent and trivalent chromium is generally found in groundwaters, surface waters, and soil solutions associated with ultramafic and mafic geologic settings (Chrysochoou et al., 2016). A natural source of Cr(III) is a chromite ore containing 45-80% percent of chromium (Coetzee et al., 2020). The sources of hexavalent chromium in the environment are primarily anthropogenic; however, it also can occur naturally in ores. Industrial processes such as leather-tanning and smelting-related chromium usage are the primary cause of Cr(VI) discharge (Ball & Nordstrom, 1998). Besides human activities, there are some geogenic processes such as weathering of ultramafic and metamorphic rocks that influence the Cr(VI) release into soil and water bodies. However, the impact of these processes is to a lesser extent compared to industrial activities (Tumolo et al., 2020).

Most chromium is found in ultramafic rocks in variable concentrations; they are also found in secondary geochemical environments such as specific soils and related waters (Oze et al., 2004; Guertin et al., 2004). Chromium is more abundant in the mafic-ultramafic rocks than in Earth's crust and waters. However, in low pH waters, such as acid mine drainage, chromium concentrations are increased (Stefansson et al., 2015).

2.1.2 Chromite deposits

Chromium ore deposits are classified into two main types (Stowe, 1994):

I. Podiform chromite deposits usually accumulate in ultramafic (olivine/serpentine-rich) parts of ophiolites or Alpine peridotites. The deposits are uneven and massive in shape (Mosier et al., 2012). Kazakhstan, Turkey, and Russia are essential producers of chromium metal.

II. Stratiform chromite deposits are hosted within mafic-ultramafic layered igneous complexes. The classic example of a stratiform chromite deposit is the South African Bushveld Complex, which has most of the world's chromite resources. The chromite intrusions are typically lens-shaped (Schulte et al., 2010).

Tectonic regimes have changed over time along with the evolution of Earth, and as a result, the settings that favor chromite concentration and deposit development have also altered. There are five tectonic settings where chromite can accumulate: i) Continental Bushveld-type layered complexes; ii) Ophiolitic crustal cumulates; iii) Podiform orebodies in the mantle tectonites; iv) Archcan greenstone belts; v) Archean layered anorthosite and ultramafic complexes in high-grade gneisses (Stowe, 1994).

2.1.2.1 Podiform chromite deposits

Podiform chromite deposits are chromite bodies developed in ultramafic portions of ophiolitic complexes within the oceanic lithosphere, upper mantle, or ophiolites. The ophiolites are interpreted as remains of old oceanic crust and upper mantle, which have not been subducted into the oceanic plates (Dilek & Furnes, 2014). As a consequence of the unstable setting in the oceanic crust, the chromite deposits are irregular in shape and elongated (Stowe, 1994). According to Wells (1940), the chromite concentrations were named “pods” because of their shape, and Thayer (1960) subsequently referred to them as “podiform”. The host rocks of chromite ore bodies are dunite, serpentine, or peridotite (Mosier et al., 2012). They all are ultramafic igneous rocks and are derived from an upper mantle. Major constituents of peridotites are olivine and pyroxene, while dunite is a type of peridotite rich in olivine and may include chromite, spinel, and pyroxene. The serpentine rocks are produced due to a hydrous alteration of ultramafic rocks, including peridotite or pyroxenite, at low temperatures (Chrysochoou et al., 2016). They are composed of serpentine group minerals such as antigorite, chrysotile, and lizardite. Apart from chromite ores, podiform chromite deposits typically carry low-grade mineralizations of platinum-group elements. Cr-rich chromitite orebodies reach a length of 1500 m and 150 m in thickness, and they are found in highly depleted harzburgitic and dunitic mantle rocks.

2.1.2.2 Stratiform chromite deposits

Stratiform chromite deposits are usually found in ultramafic, lower sections of layered intrusions, and they are expressed as massive chromitite bodies (Lee, 1996). The intrusions in stratiform deposits are laterally elongated saucer or funnel-shaped, with diameters ranging from 2 to 180 km and thickness of up to 15 km (Schulte et al., 2010). The formation of stratiform chromitites is associated with the upwelling of basaltic lava, which then intrudes into the continental crust. The principal host rocks of deposits are cumulate pyroxenite and harzburgite, and the other may include interchanging layers of dunite, lherzolite, and gabbro. Between the multiple stratiform chromite deposits and within the same layered intrusion, there is significant lithological heterogeneity. Besides chromium, the stratiform chromite deposits are also rich in platinum group elements, which include platinum, osmium, rhodium, iridium, and ruthenium (Schulte et al., 2010).

2.2 Generalities on chromium geochemistry in the environment

Chromium is a transition metal with two stable oxidation states present in the environment: Cr(III) and Cr(VI). These two species differ in terms of biogeochemical characteristics and toxicity. Due to their different properties, it is crucial to evaluate the risk of environmental damage chromium species can cause. The trivalent state of chromium is considered less soluble and less toxic in the environment, and it biologically behaves as an essential micronutrient. In contrast, the hexavalent state of chromium is a highly toxic and highly soluble metal and is regarded as a Group-I human carcinogen (Stefansson et al., 2015; Das et al., 2021).

Different chemical and physical activities, including complexation, hydrolysis, and redox reactions, affect chromium-III presence, concentration, and forms in a specific environment compartment. Cr(III) occurs as hexa-aquachromium(3+) and its hydrolysis products in the absence of complexing agents other than H_2O and OH^- (Ismael, 2014). Chromium-VI is often found in the environment. However, it is unstable when it comes into contact with electron donors like Fe(II) and organic matter with oxidizable groups. In the presence of oxygen Cr(VI) is commonly found as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions. In natural waters, the primary forms of Cr(VI) are CrO_4^{2-} and $HCrO_4^-$ (Kota &

Stasicka, 2000). On Figure 2 it is illustrated that Cr(VI) concentration increases over depth which could be correlated with dissolved silica. Moreover, hexavalent chromium is more prevalent in oxygenated waters while trivalent species increase in anoxic environmental conditions (Cranston et al., 1978).

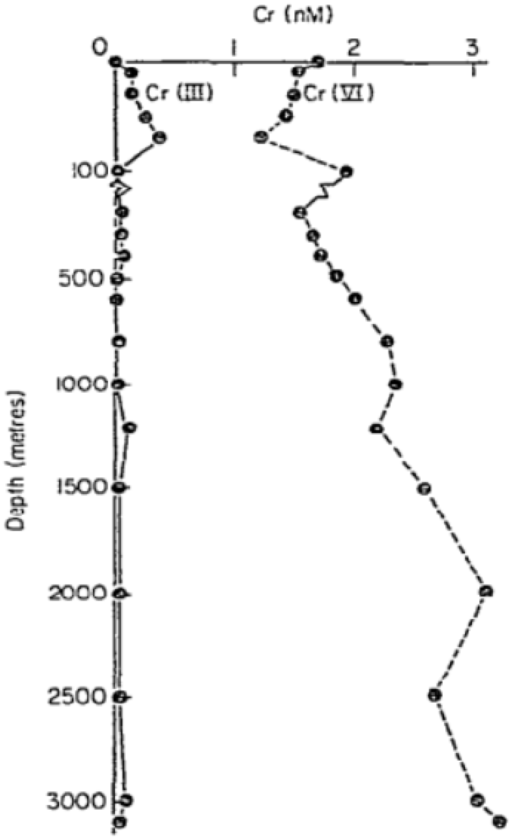

Figure 2 - Concentration of Cr with relation to depth (Cranston et al., 1978)

Trivalent chromium is strongly hydrolyzed in an aqueous solution, and its species are produced based on pH and redox potential. The trivalent Cr species are predominant under acidic conditions, and the hexavalent ones are released when the pH is basic (Oze et al., 2004).

2.2.1 Transport of chromium in natural waters

Trivalent chromium is expected to be transported less readily than hexavalent one because Cr(III) minerals precipitate in neutral to alkaline pH conditions. So several mechanisms control the transport of Cr(VI), one of them being reducing hexavalent state to trivalent state and adsorption. Reduction of Cr(VI) is likely to occur in Fe(II) conditions where it results in aqueous trivalent chromium having its concentration controlled by chromium minerals that precipitate. In that case, Cr(VI) does not migrate significantly

(Richard and Bourg, 1991). In groundwater systems, the migration of hexavalent chromium through the aquifers has been observed. The research results show that the transport velocity of chromium is highly affected by flow rate. The movement of chromite is also affected by pH and the concentration of anions in the system. Chromium migration is delayed if the pH is low and anion concentration is low. Oxygen availability in the aquifer is also vital in the migration of hexavalent chromium because, in the anoxic part, the reduction of Cr(VI) to trivalent species is taking place, which prevents the migration of chromium due to the disappearing of the hexavalent state (Richard and Bourg, 1991).

2.3 Geographical and geological setting of Aktobe region chromite mines

2.3.1 Ural mountains and Kempirsay massif

The Urals have a long history of chromium exploration and recovery, contributing over half of the world's chromite ore output, making them the second-largest chromium producer behind South Africa's Bushveld complex (Stowe, 1994). The Ural mountain range runs from north to south, forming a joint along a significant fault in Eurasia. More precisely, it covers western Siberia and underlies an extensive part of northwest Kazakhstan. According to the authors Ivanov and Rusin (1986), the Ural mountains were formed due to a collision in the Palaeozoic era between the European and Siberian-Kazakh plates. The Urals extend for approximately 2500 km along the border of Kazakhstan. Topographically the mountain range is divided into southern, northern, and central parts (Figure 3). The geological processes associated with orogeny are responsible for the formation of the diverse forms of mineralization found in the Urals.

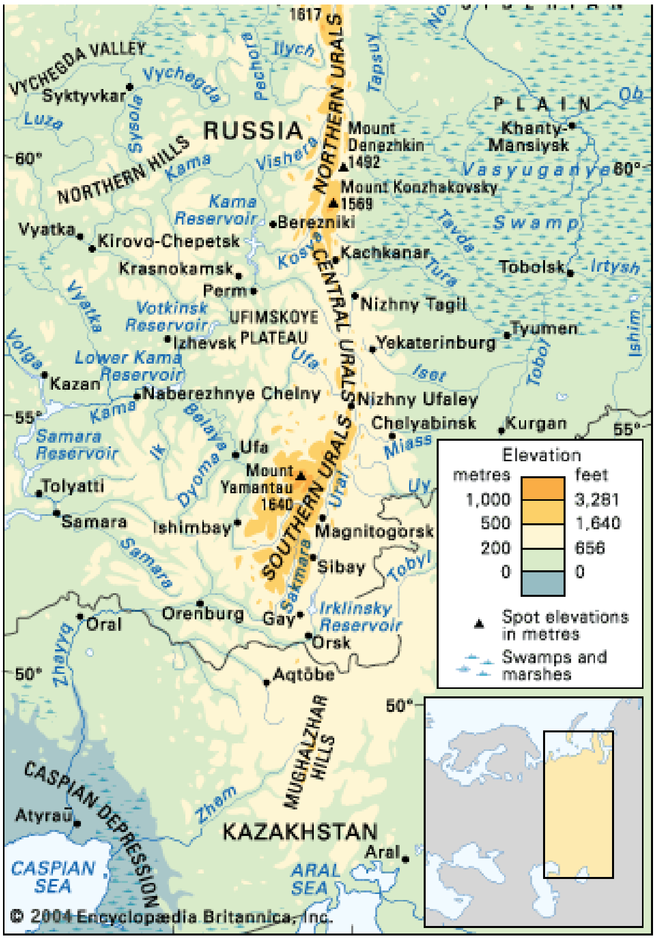

Figure 3 - The division of the Ural Mountains (Encyclopædia Britannica, 2004)

The southern part of the Ural mountains extends for approximately 550 km trending north-south from the river Ufa and terminates in the expansive Mugodzhar hills in the Aktobe region. The characteristic feature of the Southern Urals is world-class podiform chromite deposits, which were formed during the development of the oceanic-island arc. Specifically, the ultramafic Kempirsay massif in the southern extremity is widely known for the mentioned podiform chromite deposits. It covers an area of 2000 km^2, trending 90 km in a north-south direction and 32 km east-west. According to Pavlov and Chuprynina (1966), the magmatic stratigraphy of Kempirsai massif includes a complete ophiolite sequence, ranging from the fertile mantle to depleted mantle harzburgite tectonites (including chromitites), cumulates, a sheeted dyke complex, lava flows, and ocean-floor sediments (Figure 4). Melcher et al. (1997) reported that the genesis of the Kempirsay Massif's enormous podiform chromite deposits is linked to vast amounts of volatile-rich fluids likely discharged from a hydrated subducting crust slab. The massif is divided into two parts by a shear zone in the north-south direction. As seen from the geological map below, the primary chromite deposits are hosted in the southeastern part of the massif, called the Main Ore Field. The chromitite deposits of this orefield are located nearby Khromtau city.

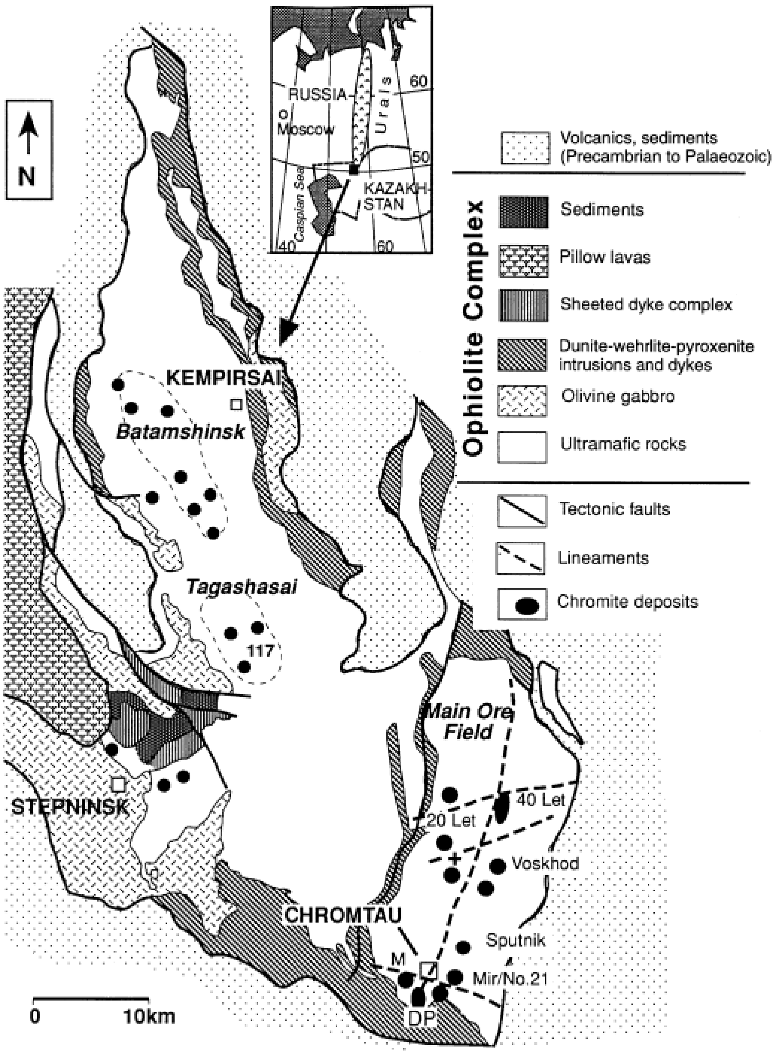

Figure 4 - Geological sketch map of the Kempirsay massif (Melcher et al., 1997)

2.3.2 Deposits near Khromtau city

The podiform chromite deposits located near the city of Khromtau are the biggest and of the highest grade of all the deposits within Kempirsay massif. Five deposits, including Almaz-Zhemchuzhina, Pervomaiskoye, Millionnoye, 10th Anniversary of Kazakhstan Independence Shaft (DNK), and No.21, lie adjacent to the city (Figure 5). Each deposit contains lenses and pods of different sizes and depths, and their in-situ grade is between 44-52% Cr_2O_3 (SRK Consulting, 2018). The chromite deposits in Millionnoye, DNK, and No.21 are primarily serpentinized pyroxenites and dunites, whereas Almaz-Zhemchuzhina and Pervomaiskoye are gabbro amphibolite.

Serpentinites are metamorphic rocks composed of serpentine group minerals such as antigorite, chrysotile, and lizardite, and these minerals are produced as a result of a hydrous alteration of ultramafic rocks at low temperatures (Chrysochoou et al., 2016). Serpentinite is a metamorphosed ultramafic rock (peridotite, pyroxenite, dunite). The serpentine soils are the soils that are derived from ultramafic rock. That type of soil is characterized by Cr concentrations of more than 200 mg/kg, significantly higher than non-serpentine soils. A common source of Cr in these types of soils are chromite and Cr-magnetite (Oze et al., 2004).

2.4 Health effects of chromium and environmental contamination

Several reports show that the mining industry is a significant polluter of the environment, and water bodies get contaminated to a large extent. The heavy metal particles can adhere to the ground surface, thus contaminating surrounding lakes and rivers and leaching into groundwater and soil (Das et al., 2021). Apart from water, chromium is also a pollutant of air through dust or fumes produced during chromium processing. Since chromium is recognized as a metal of great importance with applications in various industries, it has grown in demand in the last decade. The toxicological effect of hexavalent chromium on people, plants, and animals residing in and near mining sites has been studied extensively. Human exposure routes to chromium are skin contact, inhalation, and ingestion. Moreover, trivalent and hexavalent chromium have been found to accumulate in human and animal tissues (Das et al., 2021).

The most significant problem associated with hexavalent chromium toxicity is the pollution of natural waters and groundwaters. Since the water is consumed by both people and animals and for irrigation purposes, exposure to toxic chromium increases. Using the exposed groundwater for washing and drinking may lead to various skin diseases. Moreover, the water used to irrigate crops can harm their development. According to the World Health Organization International Standards, the acceptable level of hexavalent chromium in water is 0,05 mg/L.

2.5 Reduction strategies of Cr(VI)

The hexavalent chromium generated from industrial waste is highly toxic, and it cannot be destroyed from the water bodies and soils. The best-known disposal strategy for chromium-enriched wastes and wastewaters is the frequent reduction of Cr(VI) to a less dangerous Cr(III), and the other method is physical removal by excavating soil or pumping and treating groundwater. Some of the methods used for chromium reduction may include chemical reduction techniques, such as iron precipitation and ion exchange, and the biological technique used is microbial reduction.

2.5.1 Bacterial reduction

Microorganisms can be used to recover various contaminated settings due to their extensive metabolic diversity. Due to their tremendous adaptability and expected availability, bacteria, in particular, constitute an up-and-coming and cost-effective resource for chromium removal (Fendorf, 1995). They can potentially decrease the poisonous state of hexavalent chromium to the less harmful trivalent state, both as a survival strategy and as a method of obtaining metabolic energy for cell development (Satarupa & Paul, 2013). However, not all bacteria which are Cr(VI)-resistant can convert Cr(VI) to Cr(III) since their development is considerably slowed at high chromate concentrations (Tumolo et al., 2020). Bioaccumulation and biosorption are two techniques for removing Cr(VI) that use bacterial tolerance to high pollutant concentrations.

Bacteria have been shown to aid in the removal of metal species from aquatic solutions due to the adsorptive qualities of their cellular surface. Several factors influence the biosorption of heavy metal ions by living microorganisms, including the biomass amount, their surface properties, and physicochemical properties, such as pH, temperature, and initial metal ion concentration (Tumolo et al., 2020).

2.5.2 Chemical reduction

Hexavalent chromium's main chemical reducing agents are zerovalent iron and ferrous compounds (Fendorf, 1995). Generally, the most widely used zerovalent metal for environmental remediation is zerovalent iron. It is used as a reductant and can convert (degrading) or sequester a wide range of pollutants in both groundwater and soil (Shi et al., 2011). The species of Fe(II) will not only decrease the amount of Cr(VI) but will also increase the aqueous Cr(III) removal. Besides, the creation of solid trivalent chromium reduces the possibility of its transition back to hexavalent chromium (Fendorf, 1995). The following generic reaction can be used to represent the reduction of Cr(VI) by Fe (II) (aq):

$$Cr\ (VI)\ (aq)\ +\ 3Fe\ (II)\ (aq) \rightarrow Cr\ (III)\ (aq)\ +\ 3\ Fe\ (III)\ (aq)$$

The end products of this reaction are Cr(III) and Fe(III) species precipitated in an acidic solution, where the Fe(III) can also be toxic in the water bodies. However, the impact of chemical reduction on the environment and microorganisms are rarely explored.

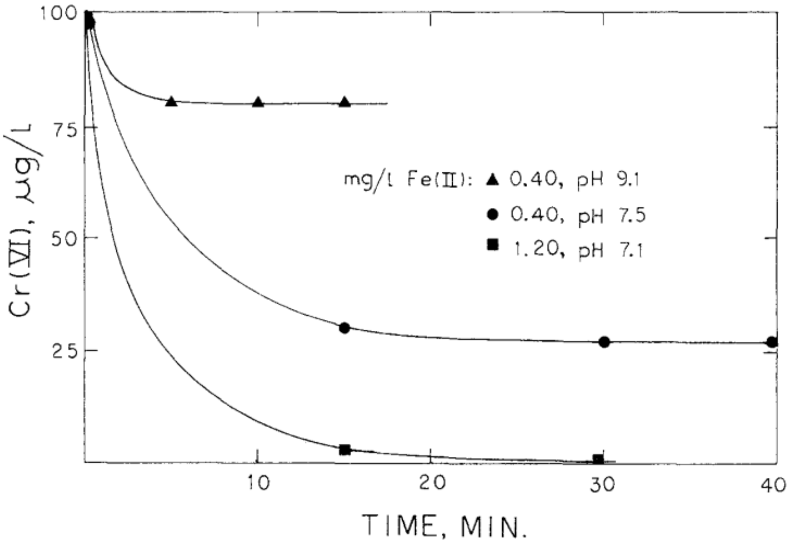

Figure 5 - Reduction of Cr(VI) by Fe(II) (Schroeder & Lee, 1975)

The reduction of hexavalent chromium can also be carried out by sulfides produced by the decomposition of organic matter and discharge of particular industrial wastes. The Cr(VI) is rapidly reduced by sulfides so that half of the chromium was reduced in less than five minutes in the presence of 10^{-3} M total sulfides (Figure 6). After five minutes, the reaction rate decreases and completes after around 27 hours. In this case, just like Fe(II), sulfides are oxidized by oxygen; however, the rate is considerably lower in comparison with the reduction by iron.

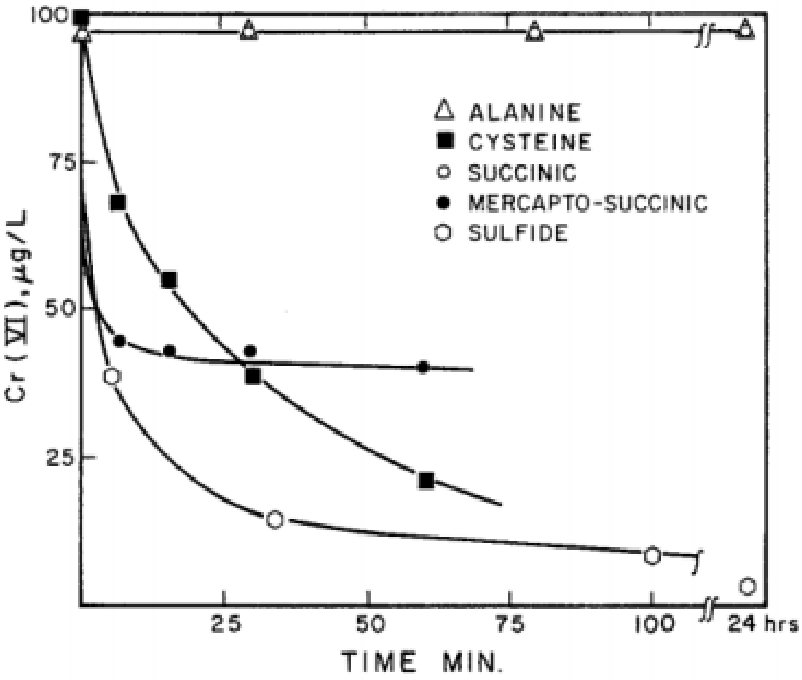

Figure 6 - Reduction of Cr(VI) by sulfides (Schroeder & Lee, 1975)

2.5.3 Ion exchange

Ion exchange is a proven technology for removing small amounts of chromium. Cr(VI) removal is best accomplished with anion exchangers, whereas Cr(III) is removed with cation exchangers (Coetzee et al., 2020). Strong-basic anion exchangers with an exchangeable counter ion of Cl- are often applied to remove Cr(VI). Since chromate is the most desired of the common anions found in water, anion exchange using synthetic resins is an ideal approach for chromium removal (Tumolo et al., 2020). Strong anionic resins include DOWEX 1, IRA-900, and Amberlite IR, which were already used in chromium removal (Beszedits, 1988). Moreover, for the removal of Cr(III), cationic exchange resins are used (e.g., Amberlite IR-120, IRN77, and SKN1). Due to the positive charge of Cr(III) and negative charge of Cr(VI), a two-step ion exchange procedure using a cation resin for Cr(III) removal and an anion resin for Cr(VI) removal may be successful if both species were present. An Illinois chrome-plating company used ion exchange water treatment. The procedure starts with the wastewater passing through a column containing Amberlite IR-120 cation exchange resin, which removes iron, nickel, trivalent chromium, and other cations, before passing through a second column containing Amberlite IRA-402 anion exchange resin, which removes hexavalent chromium, fluoride, and other anions (Beszedits, 1988).

2.6 Screening factors for chromium reduction methods in Khromtau

For the purpose of applying chromium remediation methods, several factors such as pH of water bodies and soils, temperature conditions, and Cr(VI) concentration in water bodies and soils of the Khromtau region need to be examined. The screening is done to set an optimum condition for efficient Cr(VI) reduction.

Temperature conditions are essential to identify the effectiveness of proposed remediation methods if they are implemented. Following Kazhydromet's environmental monitoring, the Aktobe region has a continental climate with wide seasonal variations in temperature. On summer days, the temperature can reach a high of 45°C and have an average temperature of 30°C. During winters, the lowest temperature is -48°C, and the daily average minimum temperature is -16°C.

According to recent research by Berdenov et al. (2018), the pH of soil samples taken near the chromium mining sites ranges between 6.8 and 9.0. Soil cover in natural and slightly polluted study areas varies from pH of 6.8 to 8.1, while in anthropogenically modified soils, pH values range between 7.7 and 9.0, which is a noticeable shift to alkaline pH. Hydrographic conditions on the territory of the Aktobe region have their characteristics. The groundwater and surface waters there are considered polluted, as stated in the national report on the state of the environment (The Ministry of Energy of the RoK, 2016). Therefore, the pH of surface and ground waters is also high as in soils. Shallow rivers and salt lakes are not suitable for the economic purposes of the city; hence fresh groundwater is used widely. The examined Ilek river basin is the most provided with surface and underground waters and is used by the Khromtau region also. However, outside the Aktobe region, the Ilek river continuation is considered highly polluted since the chemicals flow further to the tributaries. The part of the Ilek river flowing near Khromtau city has a pH ranging between 10-12.9, which is considered very alkaline (Zhakashov et al., 2011). In general, the various chemicals and pollutants cause extremely low or high pH levels in soils and waters.

The soil samples from the research sites were also examined for chromium concentration levels. Soils from areas that are located nearby the open-pit mines show a high concentration of Cr(VI), varying between 2.88-3.8 mg/L. The soils farther from the mine site have Cr(VI) concentrations of 1.1-2.8 mg/L (Berdenov et al., 2018). The high level of soil pollution near mining production is probably associated with wind erosion. The rivers flowing near the Khromtau region are also polluted since the wastewater is usually discharged into the water without treatment; tailing dams around mines contain toxic compounds and can be washed with rain, consequently causing water pollution. The concentration of hexavalent chromium in waters of the Ilek river reaches 2.2 mg/L. Kosestek, Kobda, Emba, and Or’ rivers are also considered as highly contaminated with Cr(V) levels of 0.169-2.0 mg/L in groundwaters, while the recommended level of hexavalent chromium cannot exceed 0.05 mg/L (The Ministry of Energy of the RoK, 2016).

3 PROJECT PLAN

Table 1 - Plan of research project

BSc Thesis-semester 1		August		September				October				November				December				January				February				March				April			
Stages of research (weeks)		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
1.1	Defining the area of research	🟦	🟦	🟦																															
1.2	Critical analysis of the papers				🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	
1.3	Draft submission																			🟥	🟥														
1.4	Collection of thermodynamic data																			🟩	🟩	🟩	🟩	🟩											
1.5	Preliminary geochemical modeling diagrams																								🟪	🟪	🟪	🟪	🟪	🟪					
1.6	Interpreting the geochemical data																														🟦	🟦	🟦	🟦	
1.7	Final thesis submission																																		🟥

4 METHODOLOGY

4.1 Geochemical modeling basic principles

Geochemical modeling calculations allow simulating in a quantitative manner the evolution of a water-rock system initially out of chemical equilibrium towards a state of minimum Gibbs energy of that system. These calculations are based on the laws of thermodynamics and may take into account kinetic rate laws to describe the time-dependence of heterogeneous reactions (dissolution and precipitation reactions of rock-forming minerals). Because the number of equations to be solved is extensive, geochemical modeling calculations require computer software, the most popular of which being SUPCRT92 (Johnson et al., 1992) and Geochemist's Workbench. This software can be used with different thermodynamic databases.

Geochemical software carries out two kinds of calculations: speciation and mass transfer calculations. Specifically, speciation calculations allow determining the distribution of the various chemical species at equilibrium in an aqueous solution at fixed values of temperature, pressure, pH, and redox potential (Eh). Moreover, geochemical models can simulate various types of reactions graphically, including acid-base and redox reactions.

4.1.2 Calculation of Eh-pH diagrams

The Eh-pH diagrams, also called Pourbaix diagrams, depict the stability of minerals and the prevalence of aqueous species in chemical systems. This geochemical diagram can evaluate if a mineral is in equilibrium with its environment or is undergoing chemical change. The Eh-pH diagram is built with the premise that the system is in balance with water, or instead with the three fundamental components of water, H(+1), O(-2), and e(-1).

The Geochemist's Workbench software contains an Act2 program, which plots Eh-pH diagrams. Before constructing the diagram, several calculations using thermodynamic data should be made. The calculations are automatically made in the Geochemist's Workbench software using thermodynamic data from the SUPCRT92 database.

4.2 Screening criteria of chromium remediation methods

The optimum method for hexavalent chromium treatment in surface and groundwaters in the Aktobe region is chosen by comparing the most effective proposed approaches and assessing the compatibility of methods with chromium conditions in the researched area. According to the literature review, three main methods of chromium reduction were suggested: bacterial reduction, chemical reduction, and ion exchange. Those methods are assessed by Cr(VI) concentrations in soil and water bodies, weather conditions, and pH environment.

5 DATA ANALYSIS AND RESULTS

5.1 Development of a pe-pH diagram

pe-pH diagrams are used in geochemistry to determine the predominant aqueous species of a given element as a function of pH, redox potential, and composition of the aqueous solution. The minerals' stability field can also be portrayed in these diagrams by specifying the total concentrations in the solution of the chemical elements forming these minerals. Some preliminary diagrams have been reconstructed to compare the relative stabilities of Cr(III) and Cr(VI) species.

Chromium occurs predominantly under two oxidation states in the environment: a trivalent Cr(III), which is relatively insoluble and less toxic, and a hexavalent state Cr(VI), which is the oxidation state under which aqueous solutions can transport chromium, and it is soluble and highly toxic to the environment. Moreover, these species can transform into each other by transferring electrons. The predominance of a given oxidation state for an element depends on the redox conditions prevailing in the aqueous environment. The redox relations between minerals and aqueous species are depicted in pe-pH diagrams or Eh-pH diagrams.

The stability field of water at 25°C and 1 bar is determined by the reaction:

$$2H_2O_{(l)} = 2H_{2(g)} + O_{2(g)}$$

This overall redox reaction is the sum of two half-reactions:

$$2H_2O_{(l)} = 4H^+ + O_{2(g)} + 4e^-$$

$$H_{2(g)} = 2H^+ + 2e^-$$

Where the first reaction represents the upper stability limit of water (i.e., under oxidizing conditions), and the latter represents the lower stability limit of water (i.e., under reducing conditions).

The stability field diagram for Cr(III) oxide has been established based on Figure 7 and thermodynamic values obtained from Ball and Nordstrom (1998). The reactions include:

$$Cr^{3+} + 4H_2O \rightleftharpoons HCrO_4^- + 7H^+ + 3e^-$$

$$Cr^{3+} + H_2O \rightleftharpoons CrOH^{2+} + H^+$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$$

$$CrOH^{2+} + 3H_2O \rightleftharpoons HCrO_4^- + 6H^+ + 3e^-$$

$$CrOH^{2+} + H_2O \rightleftharpoons Cr(OH)_2^+ + H^+$$

$$Cr(OH)_2^+ + H_2O \rightleftharpoons Cr(OH)_{3(aq)} + H^+$$

$$Cr(OH)_{3(aq)} + H_2O \rightleftharpoons Cr(OH)_4^- + H^+$$

$$Cr(OH)_2^+ + H_2O \rightleftharpoons HCrO_4^- + 5H^+ + 3e^-$$

$$Cr(OH)_{3(aq)} + H_2O \rightleftharpoons HCrO_4^- + 4H^+ + 3e^-$$

$$Cr(OH)_{3(aq)} + H_2O \rightleftharpoons CrO_4^{2-} + 5H^+ + 3e^-$$

$$Cr(OH)_4^- \rightleftharpoons CrO_4^{2-} + 4H^+ + 3e^-$$

Based on the reactions the ΔG and logK values have been automatically calculated for each reaction and it helped to determine the pe and pH values (Figure 7).

The blue lines on the pe-pH diagram below show the stability limits of water (Figure 7). The redox potential (pe) is shown to have a crucial influence in controlling the chromium species that prevail in solution. Even under oxidizing circumstances, all chromium exists as Cr^{3+} at pH levels of about 1. $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_{3(aq)}$, and $Cr(OH)_4^-$ are the most common Cr(III) species found in water, and their abundance varies on pH. $Cr(OH)_2^+$ species are the most prevalent in groundwaters, with a pH between 6 and 8. The dominant Cr(VI) species include $HCrO_4^-$ and CrO_4^{2-}; sometimes the solutions contain $Cr_2O_7^{2-}$ dichromate species, but only in strongly acidic solutions.

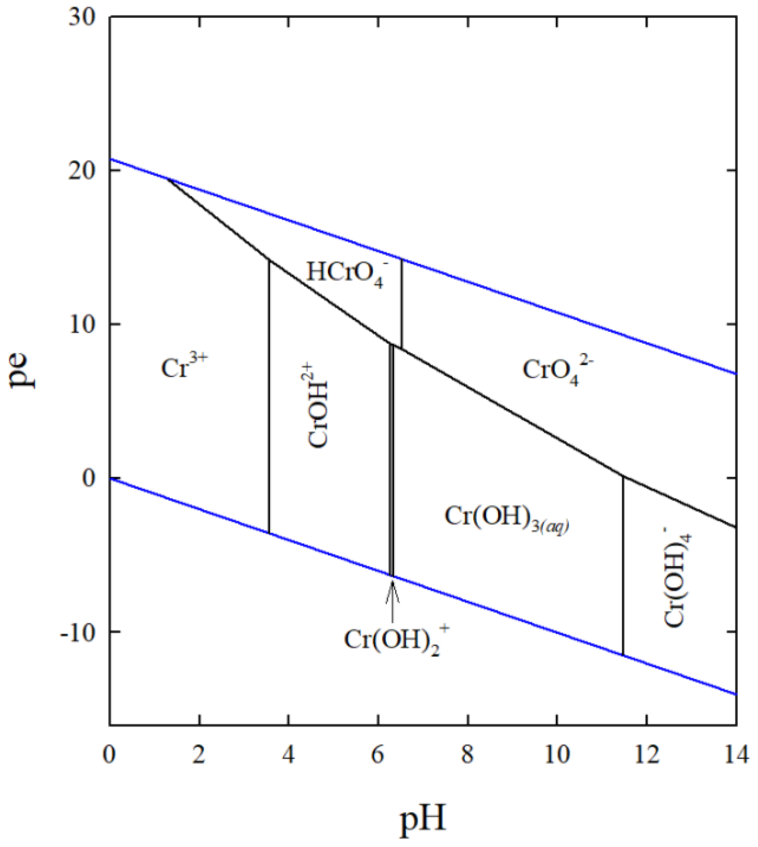

Figure 7 - pe-pH diagram at 25°C and 1 bar showing the predominance fields of aqueous species in the Cr-O-H system (reproduced after Ball & Nordstrom, 1998).

5.2 Application of Cr(VI) remediation strategies in the Aktobe region

Treatment methods available for removing chromium from water can be classified into three main groups: physical, chemical, and biological remediation. Explicitly, bacterial reduction, chemical reduction, and ion-exchange methods are discussed in this thesis. The majority of these technologies effectively remove hexavalent chromium at high concentrations. However, chromium concentrations in groundwater settings are significantly lower; the goal is to reduce them to levels below the drinking and household usage water quality requirements.

5.2.1 Bacterial reduction

The bacterial reduction of hexavalent chromium reduction is currently one of the most eco-friendly and superior alternatives over other chemical methods. The method's sustainability is significant since the pollution level in Khromtau is way beyond normal conditions. A large number of bacteria and other living organisms are capable of reducing Cr^{+6} to Cr^{+3} in both in situ and ex-situ conditions. Reduction results in Cr(III) and an organic product. Moreover, most soils and water bodies in mine sites have their indigenous microbiota, which might show tolerance to toxic chromium. The reduction process needs to be speeded up by adding more of those bacteria types. Most bacteria grow best around pH values of 6.5-7.0, but several alkali-tolerant (alkaliphilic) microbes flourish in primary 7.5-10 pH conditions. The alkaliphilic bacteria used in Cr^{+6} reduction include *Bacillus* and *Alkalibacterium* strains. This capacity of bacteria to survive is of widespread importance in industrial settings such as in Khromtau because anthropogenic pollutants increased the pH of soils and waters up to 12.9. However, the alkaline pH can affect the Cr(VI) reduction rate. With pH beyond 7, the chromium reduction rate decreases due to the osmosis and hydrolyzing effect. Nevertheless, this limitation is not essential since the chromium concentrations are not extremely high, yet it is still toxic for household use and drinking. Overall, the conditions to grow bacterial strains in Khromtau are satisfying due to the favorable temperature values, ranging between 30-40°C. Another advantage of bioremediation is its low cost and feasibility. It is crucial since the areas polluted by hexavalent chromium are extensive.

5.2.2 Chemical reduction

Chemical reduction is one of the most effective methods of Cr(VI) reduction in wastewater, and it has been observed that with Fe(II) sulfate, the removal is 100% perfect. The reason for this is a two-phase treatment: reduction by Fe(II) and subsequent precipitation of $Cr(OH)_{3(aq)}$. Moreover, while reducing the Cr(VI) compounds, Fe(II) ions are oxidized to Fe(III) compounds, which are excellent coagulating agents. Further, the formed Fe(III) hydroxides cause the Cr(III) compounds to coagulate. However, the removal of chromium by coagulation-precipitation is pH-dependent. Reduction is made under acidic conditions, whereas the pH of water bodies in Khromtau is more alkaline. Sodium hydrosulfite can be directly used in alkaline conditions, but usually, it is not cost-effective. In soils polluted by chromium, remediation by chemical reduction is not feasible due to the enormous expenditure of labor and ineffectiveness. Zerovalent iron and Fe(II) compounds are readily available and low-cost reducing agents for Cr(VI) removal, although the ecotoxicological effects on native microorganisms are rarely considered. The pollution of Khromtau is already in such deteriorated conditions that it cannot afford the generation of other pollutants. Consideration of temperature is not important, since it does not affect the chromium reduction rate and efficiency of chemical reduction.

5.2.3 Ion exchange

Ion exchange is a chromium physical remediation method that includes the construction of barriers with technical approaches. According to the EPA's recommendation for chromium removal, ion exchange is one of the best available methods. It is a reliable technology for removing low chromium concentrations, which is effective to use in Khromtau. The difficulty associated with this method includes the separate removal of Cr(VI) and Cr(III), where the first is removed with anion exchangers and the latter with cation exchangers. As the waters in the Khromtau region are primarily alkaline, present hexavalent species are chromate compounds, preferred mainly by anions. The pH of water bodies is not of great importance since the synthetic resins used as filters can be chosen considering the water pH. Temperature screening has a negligible effect on ion exchange Cr(VI) reduction. The resin regeneration process might be considered a main limitation of the ion exchange method. The resins that are fully loaded with Cr(VI) ions, which have been picked up during the cycle, have to be replaced to continue to be used again. However, this limitation will not cause any difficulty, if the synthetic resins are available in large quantities and can replace each other in an effective manner.

6 CONCLUSION

The one problem chromium causes in mining sites are toxic and carcinogenic to people's health. It is transported and is digested by the population via groundwater. The mineralogy of chromium in serpentinites includes chromite and Cr-magnetite as the primary sources of chromium and pyroxenes and chlorite as a secondary source. The aqueous geochemistry of chromium includes the concentration of chromium being variable in terms of valences. Hexavalent species increase in concentration as the depth increases. The oxygen availability also influences the concentration, so trivalent chromium is found primarily in anoxic conditions, whereas hexavalent chromium predominates in an oxygen-rich environment. The redox reactions in aqueous solutions play an essential role in chromium transport. Oxidation of trivalent chromium to hexavalent state occurs via the addition of MnO_2, whereas reduction from Cr(VI) to Cr(III) occurs by divalent iron, which results from weathering of iron-rich biotite and hematite. Also, the reduction could be carried out by sulfides that come from the decomposition of organic matter. The solubility of trivalent chromium is highly dependent on pH conditions, so it increases solubility in highly acidic basic conditions where pH is 1-4 and 10-14. At high pH conditions in perchlorate solution, the domination of hydroxo complexes has been observed. Based on the literature review, the main conclusion that can be drawn is that chromium removal from water is affected by the species of the chromium present and their concentrations and pH. As Cr(III) is insoluble at neutral and higher pH, its removal is relatively easy compared to Cr(VI) removal.

The methods proposed for chromium remediation include ion exchange, bacterial reduction, and chemical reduction. Each of these methods has different advantages and limitations. A literature review and screening criteria revealed that the most preferred method for chromium reduction in Khromtau is bioremediation. Compared to other removal methods, bacterial reduction is more sustainable and does not produce any waste. It was taken into account due to the vast pollution of Khromtau region soils and water bodies with various heavy metals other than hexavalent chromium. The main disadvantage of bacterial reduction is the long time span between the growth of bacteria and reduction. The ion exchange method can also be considered a good option for chromium reduction. However, in terms of cost, it is much higher than bacterial reduction. Accordingly, the bacterial reduction is preferred since the purification of extremely contaminated water bodies, and soils will be costly. Chemical reduction with zerovalent iron and Fe(III) is considered the most effective method, but the consequences of this treatment can enhance the deterioration of the pollution level in Khromtau. Also, the chemical reduction is preferred for the treatment of wastewater in facilities in a short time, since the reduction rate is fast compared to the other two methods. Among other proposed technologies, bioremediation and ion exchange, this method is the oldest and does not contemplate the ecological aspects of chromium removal. This research was limited in scope due to restrictions on visiting the mine sites due to the pandemic.

Further research could investigate the aquifer conditions in the groundwater system in Khromtau, Kazakhstan, and allow path tracing of the various mechanisms of chromium transport if mine site sampling of water and soil becomes possible. The chemical analysis could research chromium geochemistry in the Ilek, Emba, Kosestek, Kobda, and Or’ rivers; its concentration, mineralogy, pH and oxygen conditions, and solubility of specific chromium species could be examined. The groundwater geochemical analysis in Khromtau would provide quantitative data regarding the amount of hexavalent chromium in water. Moreover, the detailed characterization of the weathering profile of the mine site and groundwater would provide important information on chromium exposure routes.

Table 2 - Comparison of toxic chromium reduction methods

Reduction methods	**Advantages**	**Disadvantages**
Chemical reduction	Most effective for chromium removal Fast reduction rate	Fe(III) end-product that can cause pollution High cost
Bacterial reduction	Eco-friendly alternative Metabolic diversity of bacteria Low capital and operations costs	Long time-span
Ion exchange	Ease of operation Removal of both Cr^{3+} and Cr^{6+}	High cost Need to replace the synthetic resins constantly

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