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## Determination of heavy metals concentration in produced water of oil field exploration in siak regency

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**Abstract.** Oil and gas industry exploration activities produce a lot of formation water called produced water with a total of up to millions of barrels per day. Produced water from oil fields has different chemical compositions depending on geographic location, formation depth, oil production methods, and age of oil production wells. Currently, produced water is still considered as industrial waste water containing heavy metals which are harmful to humans and the environment, and require special treatment to be able to dispose of it into the environment. To determine heavy metals content in produced water of oilfield exploration, laboratory tests were performed for Siak Regency of Riau Province. Laboratory testing parameters include arsen, barium, boron, cadmium, cobalt, chromium hexavalent, iron, copper, lead, manganese, selenium, mercury, and zinc using instrument inductively couple plasma (ICP-OES) Perkin Elmer 8300DV, spectrophotometer HACH DR2800, and LUMEX RA-915. The results show the heavy metal content of  $<0,01 - 1,0$  mg/L, and only barium and boron have a concentration of more than 1.0 mg/l. Without advance treatment especially to eliminate heavy metal content, the produced water in Siak Regency is harmful as source of drinking water and other daily activity including for fisheri and crop plantation.

### 1. Introduction

Produced water is water trapped in subsurface formations that is brought to the surface during oil and gas explorations. This water has been in contact with the hydrocarbon-bearing formation for centuries, and as a result, it contains some of the chemical characteristics of the formation and the hydrocarbon itself. Produced water may include water from the reservoir, water injected into the formation, and any chemicals or surfactant added during the production and treatment processes. Produced water is sometimes referred to as brine or formation water [1].

The chemical composition of produced water vary depending on the geographic location of production area, subsurface formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. Produced water volume also vary throughout exploration time of a reservoir. If water and chemical or surfactant injections are conducted to enhance oil production, the chemical composition in produced water may vary even more dramatically.

The metals in produced water have concentration depend on the age and geology of the reservoir from which the oil and gas are produced. The common metals found in produced waters include zinc, lead, manganese, iron, and barium [2]. Discarding without proper treatment of the produced water can result in severe environmental damage and even kill the surrounding environment, kill water and plant life, and damage the soil that will affect humans [3].



Many heavy metals are identified as toxic and carcinogenic substances also gave negative impact to the human population and other living creatures in environmental. Heavy metals have a tendency for bio-accumulate in the environment and cause a negative effect on human health. When heavy metals enter the food chain in large concentrations, they may also enter and accumulate in the human body. Ingested or exposed by heavy metals in concentrations beyond the regulated limit will create serious health problems in human. The serious problem in human caused by heavy metals exposure including abnormality of growth and development, functional damage of organ, cancer, nervous system damage, and in worse case is death.

Exposure to some metals, such as mercury and lead, may develop autoimmunity and in some people the immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of foetus's brain [4].

In Indonesia, the produced water is considered as a waste and become the biggest waste from oil and gas industry which produced more than a million barrels per day, and the industry handled this type of waste by discharging after treatment to the water bodies or with subsurface injection.

Subsurface re-injection is the preferred disposal method, although it can be infeasible as the formation may not be able to receive the produced water. Injection wells are sometimes operated in concert with adjacent extraction wells to enhance recovery. A combination of produced water and other constituents is used to flood the reservoir to increase the recovery of oil and gas. This process is referred to as enhanced oil recovery, and is a common practice in the industry [5].

## 2. Method of Study

The objective of this study is to determine heavy metals concentration in produced water of oil field exploration in Siak Regency and comparing with Indonesian Government Regulation No. 82 year 2001 on the Management of Water Quality and Control of Water Pollution: stating that Class 1, water that can be used for drinking water, and or other provisions which require the same water quality; Class 2, water which the designation can be used for water recreation infrastructure, freshwater fish cultivation, livestock, water to irrigate crops, and or other uses that require the same water quality; Class 3, water for which the designation can be used for aquaculture bargaining, breeding, water to irrigate crops, and or other uses requires the same water quality.

Produced water samples were taken from each Water Injection Pump (WIP) located in Oil Gathering Station (GS) from 6 production areas in Siak oilfield with 3 replicates taken from March – April 2017. Gathering Station (GS) is a facility in each area production with separation facilities to collect fluid from production wells to separate oil, water, and gas. WIP is units for injecting produced water after separation facilities in Oil Gathering Station into oil production reservoir for enhance oil recovery (EOR) system.

To ensure quality of laboratory data, samples were taken and handled as procedure and all requirement stated in Standard Method SM 1060, also sample transported to laboratory in same day, properly preserved, and analyzed within holding time.

## 3. Laboratory Analyses of Produced Water

Produced water samples were analyzed in Technology Support Laboratory, accredited for ISO 17025 to gain quality data of heavy metals analyses for Arsenic (As), cobalt (Co), barium (Ba), Boron (B), selenium (Se) cadmium (Cd), Chromium Hexavalent ( $\text{Cr}^{6+}$ ), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), and Zinc (Zn).

Produced Water samples were filtered with 0.45  $\mu\text{m}$  and acidified with  $\text{HNO}_3$  to  $\text{pH} < 2$  then direct aspirated to Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES) Perkin Elmer 8300 DV as procedure in standard method of SM 3120 B. For mercury content, after 0.45  $\mu\text{m}$  filtration and acidified, produced water samples were analyzed using instrument Mercury Analyzer LUMEX RA-915. For  $\text{Cr}^{6+}$ , filtered samples were analyzed using HACH DR2800 spectrophotometer. As quality assurance for heavy metals analyses, instruments were calibrated with standard reference materials (SRM) and certified reference materials (CRM) were performed to check accuracy and reliability of measurement.

#### 4. Result and Discussion

The result obtained from laboratory analyses for concentration of heavy metals in produced water are collected in Table 1 along with the heavy metals limits for Indonesian Government Regulation No. 82 year 2001 on the Management of Water Quality and Control of Water Pollution.

Produced water from oilfield in Siak contained following range of mean concentration level from 6 GSs in oilfield: Barium (Ba) 1,02-2,35 mg/L; Boron (B) 5,67-7,15 mg/L; Selenium (Se) 0,03-0,04 mg/L; Cadmium (Cd) <0,03-0,01 mg/L; Chrom Hexavalent ( $\text{Cr}^{6+}$ ) 0,01-0,03 mg/L; Copper (Cu) <0,01-0,02 mg/L; Iron (Fe) 0,10-0,20 mg/L; Manganese (Mn) 0,01-0,02 mg/L, and Zinc (Zn) <0,01-0,02. For other metals have concentration below method detection: Arsen (As) <0,01 mg/L; Cobalt (Co) <0,01 mg/L; Lead (Pb) <0,01 mg/L, and Mercury (Hg) <0,001 mg/L.

**Table 1.** Result of analyses for produced water samples and No. 82 of 2001 on the Management of Water Quality and Control of Water Pollution.

Metals	Unit	Class			Mean of Concentration					
		I	II	III	GS 1	GS 2	GS 3	GS 4	GS 5	GS 6
As	mg/L	0,05	1	1	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Co	mg/L	0,2	0,2	0,2	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Ba	mg/L	1	(-) <sup>a</sup>	(-) <sup>a</sup>	1,42	1,69	1,11	1,11	1,02	2,35
B	mg/L	1	1	1	7,15	6,19	5,67	5,89	6,94	7,08
Se	mg/L	0,01	0,05	0,05	0,04	0,03	0,04	0,03	0,04	0,04
Cd	mg/L	0,01	0,01	0,01	0,01	<0,003	0,003	0,003	0,01	<0,003
Cr 6+	mg/L	0,05	0,05	0,05	0,01	0,02	0,02	0,02	0,03	0,02
Cu	mg/L	0,02	0,02	0,02	0,02	0,01	<0,01	<0,01	<0,01	<0,01
Fe	mg/L	0,3	NA	NA	0,13	0,13	0,12	0,17	0,20	0,10
Pb	mg/L	0,03	0,03	0,03	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Mn	mg/L	0,1	NA	NA	0,02	0,02	0,02	0,02	0,01	0,02
Hg	mg/L	0,001	0,002	0,002	<0,001	<0,001	<0,001	<0,001	<0,001	<0,001
Zn	mg/L	0,05	0,05	0,05	0,02	0,01	0,02	<0,01	0,02	<0,01

<sup>a</sup>Not regulated

Refer to Government of Indonesia regulation No. 82 year 2001, the heavy metals having concentration above the limit of class 1 are barium, boron, and selenium. Meanwhile for class 2 and class 3 only boron above the regulation limit.

Because of its toxic effect on plants, animals and human, heavy metals are listed in environmental pollutant category Heavy metals are persistent in nature, therefore getting accumulated in soils and plants. Dietary intake of many heavy metals through consumption of plants has long term negative effects on human health [6].

The heavy metals can have a significant impact on health also the impact on the environment. Heavy metals when entered into the body of water directly can cause special effects on living things, such as the case of minamata, damage to the nervous system, influence on fetal development, carcinogenicity and impaired immune function, so that it can be said that all heavy metals can become toxic when accumulated in the body for a long time [7].

Selenium (Se) is present in nature and often in association with sulfur containing minerals. It is normally found in concentrations of 50–90 µg/kg, but higher concentrations can be associated with some volcanic, sedimentary and carbonate rocks. Selenium is one of essential element for humans, and there are indications that selenium status may be marginal in many parts of the world. High intakes of selenium are associated with a number of specific diseases and the potential for adverse effects [8]. Even the human body actually can tolerate quite high levels of selenium without adverse effects on health. However, at high doses (>900 µg selenium/day), selenium can elicit toxic effects collectively termed

selenosis, with symptoms including gastrointestinal upset, hair loss, nausea, irritability, fatigue and mild nerve damage [9].

Barium is present as a trace element in sedimentary rocks. It is not found free in nature and occurs in a number of compounds, commonly in form of barium sulfate (barite) and to a lesser extent, barium carbonate (witherite). Barium is not a crucial element for human nutrition. High concentrations of barium will cause vasoconstriction by its direct stimulation of arterial muscle, peristalsis as a result of the violent stimulation of smooth muscles and convulsions and paralysis following stimulation of the central nervous system. Death may occur in a few hours or a few days depending on the dose and solubility of the barium salt. The acute toxic oral dose is between 3-4g [10].

Barium compounds that easily dissolve in water such as barium acetate, barium chloride, barium hydroxide, barium nitrate, and barium sulfide can cause serious health effects. Barium carbonate does not dissolve in water, but will dissolve in acidic condition in the stomach; it can also cause harmful health effects. Consuming very large amounts of barium compounds that dissolve in water or in the stomach can cause changes in heart rhythm or paralysis in humans. Some people who do not seek medical treatment immediately after eating or drinking a very large amount of barium have died. Some people who eat or drink somewhat smaller amounts of barium for a short period may experience vomiting, abdominal cramps, diarrhea, difficulties in breathing, abnormal blood pressure, numbness around the face, and muscle weakness [11].

Boron is a non-metal element in Group 13 of the Periodic Table. Properties of boron are very close to carbon and silicon. Boron is a trace element which have an important role in mineral and hormonal metabolisms, cell membrane functions, and enzyme reactions. Boron is almost completely absorbed through gastrointestinal and respiratory systems and mostly present in body tissues and fluids as boric acid  $B(OH)_3$  and in lesser amounts as  $B(OH)_4^-$  anion [12]. Boron concentration in produced water is significantly high and makes it unusable if not properly remove. The health implication of boron consumption is enormous because according to the medico-biological investigation, boron compounds belong to second class of toxicological danger [13]. Exposure to large amounts of boron (about 30 g of boric acid) in short periods of time may affect the stomach, intestines, liver, kidney, and brain and the worse is lead to death.

The lethal dose of boron (as boric acid) through gastrointestinal was reported to be 2–3 g in infants, 5–6 g in children, and 15–20 g in adults. Liver, kidney, central nervous system, and gastrointestinal effects and skin lesions have been found in lethal cases following ingestion of boron, but death has been attributed to respiratory failure [14].

Boron enters aquatic environments in many ways such a result from human activities and natural sources. Boron is soluble in water and may cause toxic effects in aquatic animals and fish are more sensitive than aquatic invertebrates to boron exposure during chronic exposures [15]. The concentration-response curve for boron is likely to be U-shaped for many species, with harm effects observed at very high and very low concentrations, while no harm effects are observed at the intermediate concentrations. The most sensitive tests report that acute effects on fish are in the range concentration of 10-20 mg/L [16].

## 5. Conclusion

This study provided information that produced water in Siak Regency contains some heavy metals with concentration above regulation limit. Without proper treatment especially to eliminate heavy metals content, produced water in Siak Regency is harmful as source of drinking water and other daily activity including for fishery and plantation based on Indonesian Government Regulation No. 82 year 2001 on the Management of Water Quality and Control of Water Pollution. Produced water injection to oil production reservoir to support enhance oil recovery (EOR) in Siak oilfield is for now the best practice of produced water management for protecting people and environmental.

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