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Short Communication

Potential mining of lithium, beryllium and strontium from oilfield wastewater after enrichment in constructed wetlands and ponds

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HIGHLIGHTS

- Produced water of oil industry is a source for rare earth elements.
- Wetlands can be used for mining of rare earth elements.
- A considerable monetary worth can be gained by use of the proposed technique.

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ABSTRACT

Shortages of resources (chemical elements) used by growing industrial activities require new techniques for their acquisition. A suitable technique could be the use of wetlands for the enrichment of elements from produced water of the oil industry. Oil industries produce very high amounts of water in the course of oil mining. These waters may contain high amounts of rare elements. To our best knowledge nothing is known about the economic potential regarding rare element mining from produced water. Therefore, we estimated the amount of harvestable rare elements remaining in the effluent of a constructed wetland-pond system which is being used to treat and evaporate vast quantities of produced waters. The examined wetland system is located in the desert of the south-eastern Arabian Peninsula. This system manages 95,000 m^3 per day within 350 ha of surface flow wetlands and 350 ha of evaporation ponds and is designed to be used for at least 20 years. We found a strong enrichment of some chemical elements in the water pathway of the system (e.g. lithium up to 896 $\mu g\ L^{-1}$ and beryllium up to 139 $\mu g\ L^{-1}$). For this wetland, lithium and beryllium are the elements with the highest economic potential resulting from a high price and load. It is calculated that after 20 years retention period 131 t of lithium and 57 t of beryllium could be harvested. This technique may also be useful for acquisition of rare earth elements. Other elements (e.g. strontium) with a high calculated load of 4500 tons in 20 years are not efficiently harvestable due to a relatively low market value. In conclusion, wetland treated waters from the oil industry offer a promising new acquisition technique for elements like lithium and beryllium.

1. Introduction

The problem of shortages in metals, metalloids and especially rare earth elements for commercial products is increasing worldwide (Feltrin and Freundlich, 2008; Hong, 2006). At the same time more and more alternative techniques are used to exploit the required elements. In the course of oil drilling and extraction very high amounts of water are lifted to the earth surface (Cheryan and Rajagopalan, 1998). After oil separation, the remaining wastewater is known in the oil industry as “produced water”. These waters often contain high amounts of chemical elements such as metals, metalloids and rare earth elements (Afkhami et al., 2013; Fiedler et al., 2009). There are several techniques for managing these waters e.g. ultrafiltration (Asatekin and Mayes, 2009). One of them is deep well disposal or re-injection in which the produced water is pumped back to the oil reservoirs or deep aquifers, consuming high amounts of energy which in turn results in high costs and high CO_2 emission (Din et al., 2009). Alternative commonly used techniques for water treatment in general are precipitation, co-precipitation or pH manipulation (Fu and Wang, 2011).

Another technique known for its low operating costs is the use of constructed wetlands. Such an approach was implemented by BAUER in 2010 in the desert of the south-eastern Arabian Peninsula. The Produced Water Treatment Plant (PWTP) uses 350 ha of surface flow wetlands to degrade residual hydrocarbons after oil separation and reduce the water volume through evapotranspiration, followed by a 350 ha series of evaporation ponds to evaporate the treated water that is not reused, with salt being the final residue at the end of the system. This wetland treatment plant is designed to operate for a minimum of

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20 years and treats 95,000 m^3 d^{-1} of produced water and functions primary as a zero liquid discharge system (i.e. no outflow). Nothing is currently known about the possible elemental harvest from such a water treatment plant to our best knowledge. However, resulting from moderate to high element concentrations in the water and vast quantity of received water, a high element accumulation within this system is expected. Consequently, we tried to determine the potential harvest sites and conducted a screening trial to identify elements present in potentially harvestable quantities over a 20 year operating period at the water treatment plant. Our hypothesis is that a high amount of rare elements can be potentially harvested from the evaporation ponds of the water treatment plant.

2. Material and methods

2.1. The produced water treatment plant

The oilfield is located in the south eastern part of the Arabian Peninsula and the oil deposit is found at a depth of about 3000 m. The water is traditionally managed after oil separation by deep well disposal underground. 95,000 m^3 d^{-1} is treated at the PWTP. The system was commissioned in early 2011 and run by BAUER. The PWTP is primarily designed as a zero-discharge system and consists of a constructed wetland which enhances the evapotranspiration by using plants with a high transpiration rate (e.g. common reed, *Phragmites australis* Cav. (Trin.) ex Steud.). The influent of produced water (PW) is treated by an oil separator and afterwards flows into an inlet distribution and buffering pond (BP) (Fig. 1). In the next step the water flows from the buffer pond into a 350 ha surface flow wetland (SFW) system divided into nine parallel streams, each with four wetland cells in series. Each SFW cell has a size of 9.75 ha. From the SFW the water enters a collection channel (CC) from where some water is extracted and reused for purposes such as irrigation and drilling water. Thereafter, the water flows into a 350 ha series of evaporation ponds (EP) where the remaining water is evaporated with salt being the final residue (Fig. 1). The whole system covers an area of more than 700 ha. The substrate layer used for the system is the onsite predominating laterite soil.

Conductivity and temperature (95 Lf, Fa WTW) as well as pH value (Electrode: Mettler Toledo INLAB 414, unit: Delta 320, Germany) was measured directly (DIN-EN-27888, 1993) in the outlets of each reed bed/buffer pond/collecting channel or within the evaporation ponds. The produced water entering this wetland has a conductivity of about 11 mS cm^{-1} and a pH of 7.9. pH values increased within the system to more than 9. Dissolved oxygen measured by Oxi-320 (WTW, Weilheim, Germany) at the inflow is low (0.4 mg L^{-1}) and increases within the system up to 10 mg L^{-1}. The conductivity increased along the whole

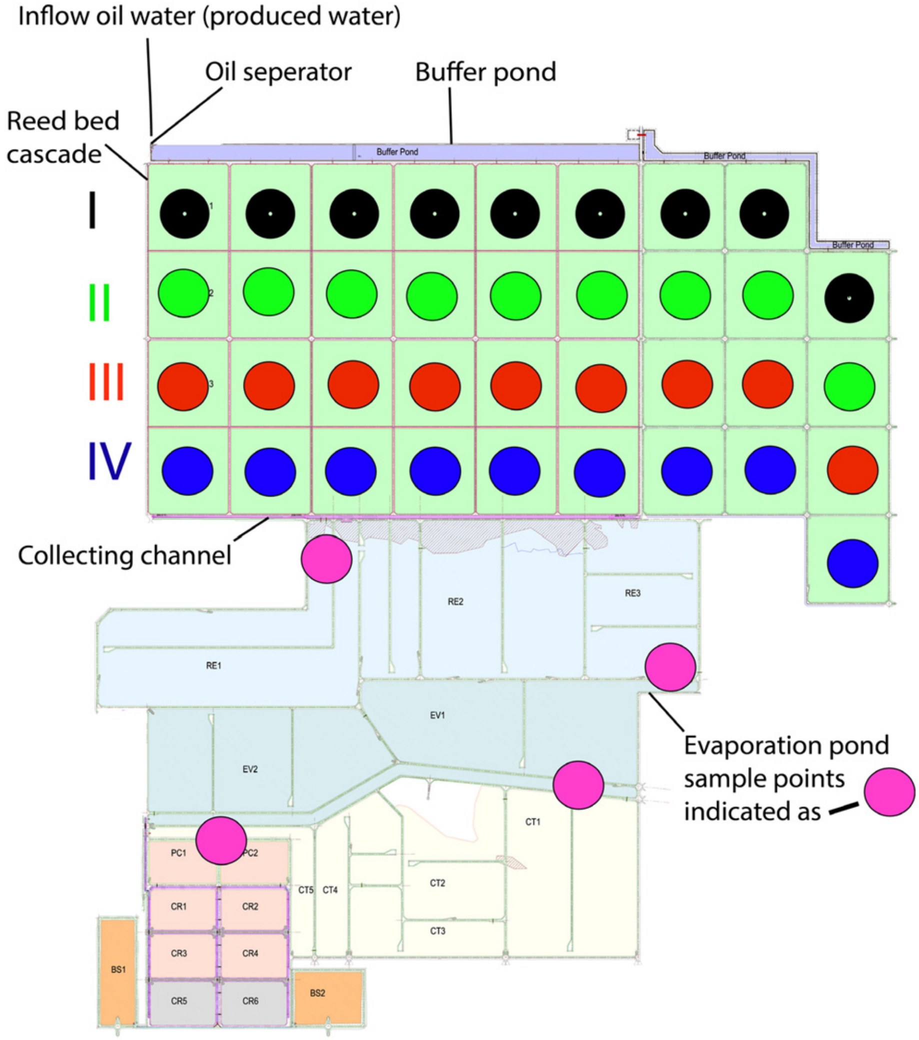

Fig. 1. Overview of Produced Water Treatment Plant and locations of water sampling within the reed bed, buffer pond and collecting channel samples, and evaporation ponds. Sampling points are figured as dots of different color. The water flow within the evaporation ponds is from RE1 to RE3, followed by EV1 and EV2, CT1 to CT5, PC1 and PC2 to the last ponds (CR1–CR6) where the elements can be harvested.

water pathway from 11 to more than 50 mS cm^{-1}. The climate in the south eastern Arabia peninsula is described as arid (Garzanti et al., 2002) with a potential evaporation of about 2200 mm per year (FAO-water-reports, 2008).

2.2. Sampling, sample preparation and analysis

Grab water samples were taken on 22/12/2011 within the different parts of the system according to Fig. 1, each at a representative plot. A volume of 20 mL of water from the produced water, buffer pond water, different SFW cells, collection channel and the evaporation ponds was randomly sampled and subsequently acidified using HNO_3 (analytical grade, Carl Roth Germany) immediately after collection (DIN-EN-ISO-5667, 2004). Inductively coupled plasma mass spectrometry (ICP-MS) measurements (PQ exCell instrument, Thermo Fisher Scientific Inc.) were used according to DIN-EN-ISO-17294-2 (2004) for metals and rare element analysis such as lithium, beryllium, magnesium, aluminum, calcium, iron, manganese, strontium and barium. Calibration functions were recorded from mixed calibration samples, which were prepared from multi-element solutions (Bernd Kraft, Duisburg, Germany). Limit of detection (LOD) was calculated as the threefold standard deviation of the instrument blank (acidified water). All chemicals were of analytical grade.

Analysis of variance (ANOVA) was applied to determine if the element concentration differed significantly throughout the system using SPSS version 14.0. Furthermore, the potential mass of elements entering the system with the produced water was estimated by calculations based on water element concentration multiplied by the amount of water inflow expected over the next 20 years of operation.

3. Results and discussion

3.1. Element concentrations within the system

A significant ($p < 0.005$) enrichment (470 %) of lithium was found within the system with up to 896 μg L^{-1} in the last evaporation pond (Table 1). Lithium is not biologically utilized according to other studies using lithium as tracer (Brenan et al., 1998). Hence, lithium is transported up to the last evaporation pond and can be harvested here. The same pattern with a rapid concentration increase in the last evaporation ponds, was found for beryllium (139 μg L^{-1}) (200% enrichment) and magnesium (225 mg L^{-1}) (580% enrichment) (both $p < 0.001$) (Table 1). Hence, these two elements are also potentially harvestable. This is in accordance with Brenan et al. (1998), describing beryllium being a good tracer. But beryllium as tracer is not as good as lithium, because of its greater adsorption to organic sediments and plant material (Willenbring and von Blanckenburg, 2010).

The concentration of manganese and iron decreased very much within the system ($p < 0.001$). This may be explained by biological uptake by reed (Brackhage et al., 2013) or the possible sorption/precipitation of these two elements into the soil. A decrease of aluminum was observed in the SFW and could be explained by sorption to organic/inorganic sediment particles (Schaller et al., 2013). No clear pattern was found for barium. Interestingly, we found no significant concentration difference for calcium and strontium throughout the system (Table 1). The lack of significance for strontium values could be explained by their high variance. The concentration pattern of calcium seems to be due to increasing pH values (up to 9), and probably resulting in carbonate precipitation (Colfen and Qi, 2001). Calcium might precipitate even in the first reed beds (Colfen and Qi, 2001; Sahai et al., 2000). Hence, harvesting calcium and strontium in the PWTP is not considered to be efficient.

3.2. Estimated element load during 20 years of operation

The highest element amounts to be potentially harvested were calculated for magnesium and calcium. With regard to their low price a harvest by wetlands maybe nevertheless meaningful. More interesting is the amount of lithium (6.6 tons/year), beryllium (2.9 tons/year) and strontium (223 tons/year) (Table 2). Beryllium, but even more so, lithium, is potentially harvestable in very high amounts within a small area of the evaporation ponds. The harvestable amount of lithium and beryllium after 20 years together is comparable with a thousandth of the global production of rare earth elements per year (Chen, 2011). Based on the market price of these elements (currently $4500 per ton for lithium (Kim et al., 2010) and $3100 per ton for beryllium (Grosjean et al., 2012; Kim et al., 2010)) the calculated price of harvestable lithium sums up to currently $590,000 and $180,000 (currently) for beryllium within 20 years of operation. The PWTP manages a relatively small amount of water compared to the water output of many oil fields (Babadagli, 2007; Wojtanowicz et al., 1994). Hence, in other oil fields much higher amounts of rare elements may be harvestable, depending on the initial concentration in the produced water. Furthermore, a considerable amount of strontium (~4500 tons) will accumulate within the PWTP during the operation time span. However, the low strontium price value (currently 68 $ per ton) is not favorable for a viable harvest at this stage.

4. Conclusion

In conclusion, using the technique of the PWTP, very high amounts of rare elements could be harvested in different oil fields all over the world. Consequently, additional value could be obtained from these systems by marketing rare elements. It is important to note that elements with chemical characteristics of inertness and biological inactivity (e.g. lithium and beryllium) are especially suitable for the use with this technique. These elements are enriched via evaporation and can be easily harvested from salt fields at the end of the evaporation ponds.

Table 1
Average elemental water concentration (+/− standard deviation) in μg per liter within the different parts of the system for produced water inflow (PW), buffer pond (BP), different terraces (1–4) of the surface flow wetlands (SFW), collection channel (CC) and evaporation ponds (EP). Furthermore, the concentration reached in the last evaporation pond (EP 4) is given in brackets. A significant enrichment from PW to EP was found for lithium ($p < 0.005$, referred as *) and for both beryllium and magnesium ($p < 0.001$, referred as #).

Element	PW	BP	SFW-1	SFW-2	SFW-3	SFW-4	CC	EP (EP-4)
Lithium	191 ± 6	186 ± 2	206 ± 7	217 ± 5	227 ± 4	248 ± 15	276 ± 8	451 ± 300 (896)*
Beryllium	71 ± 6	82 ± 2	46 ± 3	46 ± 3	48 ± 3	50 ± 2	62 ± 2	94 ± 31 (139)#
Magnesium	38500 ± 1140	37500 ± 902	38400 ± 1300	41000 ± 1060	46300 ± 3200	51500 ± 4300	58700 ± 1700	106600 ± 79000 (225000)#
Aluminum	105 ± 6	176 ± 140	113 ± 19	88 ± 5	89 ± 32	70 ± 8	58 ± 6	70 ± 5 (68)
Calcium	92700 ± 4090	100295 ± 8090	103400 ± 4500	103800 ± 4700	90600 ± 15000	67260 ± 21000	64800 ± 4400	121600 ± 14700 (341000)
Iron	136 ± 21	159 ± 80	0	0	0	0	0	0
Manganese	105 ± 3	116 ± 10	129 ± 16	91 ± 11	43 ± 27	20 ± 16	5 ± 2	12 ± 1 (12)
Strontium	6355 ± 271	6360 ± 74	6660 ± 235	7298 ± 227	7070 ± 576	6820 ± 340	7196 ± 218	11060 ± 8100 (23200)
Barium	174 ± 6	185 ± 4	208 ± 15	218 ± 8	205 ± 19	187 ± 14	172 ± 6	159 ± 22 (183)

Table 2
Expected elemental harvest from the Produced Water Treatment Plant after 20 years of operation.

Element	Ton per year	Ton per 20 years
Lithium	6.57	131
Beryllium	2.87	57
Magnesium	1266.68	25,334
Aluminum	13.57	271
Calcium	3894.70	77,894
Iron	9.60	192
Manganese	4.53	91
Strontium	223.03	4461
Barium	6.26	125

Elements which lead to a wider distribution based on their chemistry (e.g. calcium) are not suitable for harvest. This technique for rare element “mining” by the use of wetlands has a very high potential and can improve the commercial feasibility of such water management projects.

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References

Afkhami F, Karbassi AR, Nasrabadi T, Vosoogh A. Impact of oil excavation activities on soil metallic pollution, case study of an Iran southern oil field. Environ Earth Sci 2013;70:1219–24.

Asatekin A, Mayes AM. Oil industry wastewater treatment with fouling resistant membranes containing amphiphilic comb copolymers. Environ Sci Technol 2009;43:4487–92.

Babadagli T. Development of mature oil fields — a review. J Pet Sci Eng 2007;57:221–46.

Brackhage C, Schaller J, Bäucker E, Dudel EG. Silicon availability affects the stoichiometry and content of calcium and micro nutrients in the leaves of common reed. Silicon 2013;5:199–204.

Brenan JM, Ryerson FJ, Shaw HF. The role of aqueous fluids in the slab-to-mantle transfer of boron, beryllium, and lithium during subduction: experiments and models. Geochim Cosmochim Acta 1998;62:3337–47.

Chen Z. Global rare earth resources and scenarios of future rare earth industry. J Rare Earths 2011;29:1–6.

Cheryan M, Rajagopalan N. Membrane processing of oily streams. Wastewater treatment and waste reduction. J Membr Sci 1998;151:13–28.

Colfen H, Qi LM. A systematic examination of the morphogenesis of calcium carbonate in the presence of a double-hydrophilic block copolymer. Chem Eur J 2001;7:106–16.

Din SU, Oskui RP, Dusseault MB, Al Ghadban AN. Multi-criteria evaluation technique for SFI site identification of NORMS and oil industry waste disposal — possibilities in Kuwait. J Environ Manage 2009;91:186–94.

DIN-EN-27888. Water quality; determination of electrical conductivity. Berlin: Deutsches Institut für Normung; 1993. p. 16.

DIN-EN-ISO-17294-2. Wasserbeschaffenheit - Anwendung der induktiv gekoppelten Plasma-Massenspektrometrie (ICP-MS) — Teil 2: Bestimmung von 62 Elementen (ISO 17294-2:2003). Deutsche Fassung EN ISO 17294-2:2004. Berlin: Deutsches Institut für Normung; 2004. p. 24.

DIN-EN-ISO-5667. Anleitung zur Konservierung und Handhabung von Wasserproben DIN EN ISO 5667-3:2003. Berlin: Deutsches Institut für Normung; 2004. p. 49.

FAO-water-reports. AQUASTAT Survey. Irrigation in the Middle East region in figures — AQUASTAT Survey 2008In: Frenken K, editor. ; 2008. p. 423. (2008).

Feltrin A, Freundlich A. Material considerations for terawatt level deployment of photovoltaics. Renew Energy 2008;33:180–5.

Fiedler S, Siebe C, Herre A, Roth B, Cram S, Stahr K. Contribution of oil industry activities to environmental loads of heavy metals in the Tabasco Lowlands, Mexico. Water Air Soil Pollut 2009;197:35–47.

Fu FL, Wang Q. Removal of heavy metal ions from wastewaters: a review. J Environ Manage 2011;92:407–18.

Garzanti E, Vezzoli G, Ando S. Modern sand from obducted ophiolite belts — (Sultanate of Oman and United Arab Emirates). J Geol 2002;110:371–91.

Grosjean C, Miranda PH, Perrin M, Poggi P. Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry. Renew Sust Energ Rev 2012;16:1735–44.

Hong F. Rare earth: production, trade and demand. J Iron Steel Res Int 2006;13:33–8.

Kim SK, Ko WI, Kim HD, Revankar ST, Zhou W, Jo D. Cost-benefit analysis of BeO-UO2 nuclear fuel. Prog Nucl Energy 2010;52:813–21.

Sahai N, Carroll SA, Roberts S, O'Day PA. X-ray absorption spectroscopy of strontium(II) coordination — II. Sorption and precipitation at kaolinite, amorphous silica, and goethite surfaces. J Colloid Interface Sci 2000;222:198–212.

Schaller J, Vymazal J, Brackhage C. Retention of resources (metals, metalloids and rare earth elements) by autochthonously/allochthonously dominated wetlands: a review. Ecol Eng 2013;53:106–14.

Willenbring JK, von Blanckenburg F. Meteoric cosmogenic beryllium-10 adsorbed to river sediment and soil: applications for Earth-surface dynamics. Earth-Sci Rev 2010;98:105–22.

Wojtanowicz AK, Xu H, Bassiouni Z. Segregated production method for oil-wells with active water coning. J Pet Sci Eng 1994;11:21–35.