



## Characteristics and disposal options of sludge from a steel mill wastewater treatment plant

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### Original Article

#### Abstract

In the present study, sludge from a steel wastewater treatment plant (SWWTP) was analyzed regarding its physicochemical characteristics and metal contents, and disposal options. For these purposes, grab sampling was used to collect 18 slurry and 18 cake sludge samples in 6 months (May-October 2012). Mann-Whitney U test, one sample T-test and Wilcoxon signed rank test were applied to analyze the obtained data. Canadian Soil Quality Guidelines (CSQG) and Florida Department of Environmental Protection Soil Cleanup Target Levels (FDEPSTLs) were used to discuss the disposal fate of the generated sludge. The results showed that the order of the studied metals in the sludge was as: Fe>Al>Ca>Mg>Zn>Na>Pb>Mn>Cu>Cr>Ni>Co>Cd. It was found that due to higher concentration of Cu, Pb, Zn and Fe in the generated sludge, compared with CSQG and FDEPSTLs, it is not suitable for residential and non-residential applications.

**KEYWORDS:** Industrial Wastewater Sludge, Physicochemical Characteristics, Steel Mill, Disposal

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#### Introduction

Waste management has become a serious issue in many parts of the world. Management options need some extensive waste characterization operations, because many of them may contain dangerous compounds for the environment, such as heavy metals.<sup>1</sup> Heavy metals are part of many industrial sludge and they are considered as hazardous waste.<sup>2</sup> They are non-biodegradable and have tendency toward bioaccumulation in living organisms. Therefore, they can negatively affect human and animals, and also environment.<sup>3,4</sup>

There are different methods for sludge management. It can be used in agricultural lands,<sup>5,6</sup> manufacturing construction materials,<sup>2,7</sup> wastewater treatment reagents,<sup>8</sup> sludge dewatering<sup>9</sup> or land filling. Such methods in addition to their advantages, including economic savings on over all treatment plant operation costs and environmental sustainability, have some limitations such as complexity of the method and problems that can be caused by pollutants presented in the sludge and can be extracted from it. Thus, having knowledge of sludge properties is crucial in selecting the suitable disposal option.

This investigation tries to determine the physicochemical characteristics and heavy metals of the slurry and cake sludge from a steel

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wastewater treatment plant in Ahvaz, southwestern Iran. The heavy metal concentrations were compared with Canadian Soil Quality Guidelines (CSQG) for the Protection of Environmental and Human Health<sup>10</sup> and Florida Department of Environmental Protection Soil Cleanup Target Levels (FDEPCTLs).<sup>11</sup> Finally, some of sludge disposal methods were discussed.

### Materials and Methods

The studied steel wastewater treatment plant, located in the south west of Iran, has a capacity of 3000 m<sup>3</sup>/h. Figure 1 shows the WWT procedure in the studied steel wastewater treatment plant (SWWTP). Alum [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>], and polyelectrolyte (anionic polymer) are used as coagulant and coagulant aid, respectively. The sludge from DAF and Clarifier is dewatered by passing a filter press and cake sludge is produced. Cake sludge is dumped every day somewhere out of the studied site, without any analysis on its component and any consideration of public health and environmental sustenance.

In this study, that is a spatial cross-sectional analysis of sludge from a steel mill wastewater treatment plant, 36 samples, including 18 slurry sludge and 18 cake sludge samples were

collected in 6 months, May-October 2012. Slurry and cake samples were collected before and after dewatering operation, respectively, both in grab sampling manner. Samples transportation and storage were according to Standard Methods for the Examination of Water and Waste Water.<sup>12</sup>

Total solids (TS), total suspended solids (TSS), total dissolved solids (TDS) (oven Heraeus, Germany), fixed and volatile solids (FSS and VSS) (Furnace Vecstar Ltd., England), pH (pH meter Mettler-Toledo, Switzerland) and electrical conductivity (EC) (conductivity meter WTW, Germany) were determined. Metal content (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Zn) were measured by an ICP-OES HORIBA JobinYvon-ULTIMA 2 Cin the cake sludge samples. Chemical components (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, MnO, P and S) were also determined using a XRF MDX1000, England.

Metals content and chemical components were determined using ASTM<sup>13</sup> and other parameters were measured according to Standard Methods for the Examination of Water and Waste water.<sup>12</sup> All chemicals used in this study were of analytical grade. Heavy metals standards for ICP were Assurance Company production (France).

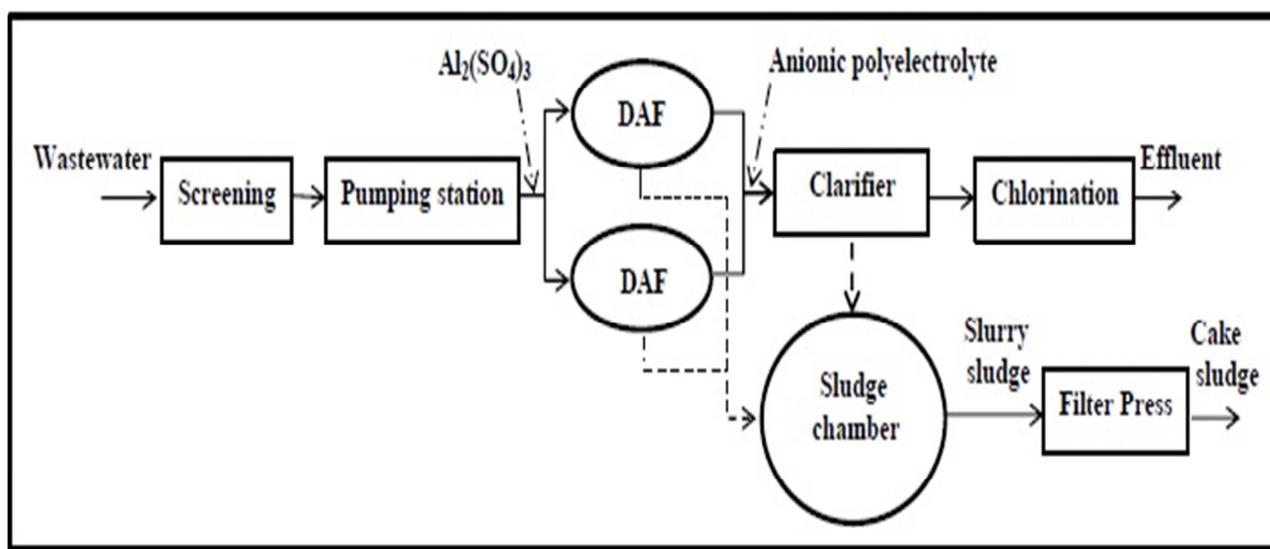


Figure 1. Treatment process of the steel wastewater in studied site

At first, samples were dried and sieved to obtain same sized particles. Then proper amount of these particles was digested with a mixture of concentrated HCl and concentrated HNO<sub>3</sub> on a hot plate. After being cooled, the samples were filtered through an ashless filter paper and the filtrate was diluted to a volume of 100 ml with deionized water.

In order to analyze the data, first of all explorer command and stem and leaf graph were used to exclude outlier data. Then, to assess the normality of the data, Kolmogorov-Smirnov Z analysis was performed. Mann-Whitney U test was used to compare non-normal distributed data. One sample t-test (for normal distributed data) and Wilcoxon signed rank test (for non-normal distributed data) were applied to compare metals concentration with the standard values. Since, there are no standards, regulations, or legal restrictions available for soil clean-up levels in Iran, CSQG and FDEPSCTLs were used for this purpose.

## Results and Discussion

### Characteristics of the steel sludge waste

Table 1 represents some physicochemical characteristics of both slurry and cake sludge in studied SWWTP. The number of samples for some parameters is less than 18, which is due to omission of outlier data. The results of Kolmogorov-Smirnov Z test introduced

distributions of sludge's physicochemical parameters as non-normal. So, Mann-Whitney U test was used for them (Table 1).

As table 1 shows, and according to Mann-Whitney U test results, TS, VSS, FSS and TSS in cake sludge is significantly higher than those of slurry sludge ( $P < 0.0001$ ). It was expected because after dewatering using filter press, solid content of the sludge is concentrated. Ahmadi et al. in their study on sludge from a petrochemical wastewater treatment plant reported a similar TSS but higher TDS for their studied sludge than that of this study.<sup>14</sup>

EC of the studied sludge was lower than that of reported by Bahremand et al. and Kassray and Saedi and Dashti et al. for their studied sludge.<sup>6,15,16</sup> Higher EC means higher salinity, which makes the studied sludge unsuitable for land application. pH has an important role in metals behavior in soil and their uptake by organisms.<sup>3</sup> pH of the studied sludge was slightly alkaline.

Table 2 represents the metal content of the studied cake sludge. As mentioned before, omitting outlier data, the number of samples for some metals is less than 18. Considering table 2, the order of the studied metals in the sludge is as follows:

Fe>Al>Ca>Mg>Zn>Na>Pb>Mn>Cu>Cr>Ni>Co>Cd

As it has been expected, Fe had the highest

**Table 1. Physicochemical characteristics and statistical results of slurry and cake sludge**

Parameter/unit	Sludge	Number of samples	Mean ± SD	Median	P
TS (%W)	Slurry	16	1.74 ± 0.47	1.72	< 0.0001
	Cake	18	34.540 ± 8.720	21.760	
VSS (%W)	Slurry	14	0.609 ± 0.086	0.630	< 0.0001
	Cake	18	11.45 ± 4.276	10.94	
FSS(%W)	Slurry	16	1.00 ± 0.31	0.98	< 0.0001
	Cake	18	23.090 ± 7.178	34.065	
TSS (mg/l)	Slurry	15	13873.53 ± 3069.03	13728	< 0.0001
	Cake	18	318481.11 ± 97110.631	329550	
TDS (mg/l)	Slurry	16	3081.09 ± 405.65	3147.5	-
EC (µs/cm)	Slurry	18	4866.780 ± 633.289	4920	-
pH	Slurry	18	7.680 ± 0.223	7.7	-

TS: Total solids; VSS: Volatile solids; FSS: Fixed solids; TSS: Total suspended solids; TDS: Total dissolved solids; EC: Electrical conductivity

**Table 2. Metal content of the cake sludge**

Metal	Unit	Number of samples	Mean $\pm$ SD	Median
Al	mg/kg dry solid	18	41432.43 $\pm$ 39131.09	34744.00
Ca	mg/kg dry solid	16	31268.75 $\pm$ 27796.29	14275.00
Cd	mg/kg dry solid	16	2.36 $\pm$ 2.82	0.70
Co	mg/kg dry solid	16	8.03 $\pm$ 8.17	2.60
Cr	mg/kg dry solid	18	57.16 $\pm$ 34.70	59.14
Cu	mg/kg dry solid	18	295.47 $\pm$ 317.56	296.32
Fe	mg/kg dry solid	16	306131.44 $\pm$ 35268.03	306048.74
Mg	mg/kg dry solid	16	11424.06 $\pm$ 10474.43	5280.00
Mn	mg/kg dry solid	17	378.47 $\pm$ 313.21	306.76
Na	mg/kg dry solid	15	3940.16 $\pm$ 2908.66	2262.66
Ni	mg/kg dry solid	13	35.54 $\pm$ 32.10	38.30
Pb	mg/kg dry solid	18	393.21 $\pm$ 306.83	357.96
Zn	mg/kg dry solid	15	6491.88 $\pm$ 3841.05	6327.00

concentration amongst the studied metals. Since  $\text{Al}_2(\text{SO}_4)_3$  has been used as the coagulant, Al had the second rank. Zn had the third and first ranks amongst the metal contents and heavy metals, respectively. Comparing our results with those of Silva et al.,<sup>2</sup> it was observed that Cu, Ni, Pb and Zn in our studied sludge were higher than those in their studied metal-mechanics, textile and automotive sludge. Considering the differences in the nature of sludge, such dissimilarity in the results can be expected.

XRF results for chemical composition of the studied sludge introduced  $\text{Fe}_2\text{O}_3$  as the main composite (30.15%) and  $\text{Al}_2\text{O}_3$  as the second composite with the highest percentage (30.15 and 11.02%, respectively). As mentioned before, Fe and Al are two metals with the highest concentration in the studied sludge (See table 2). Then, such result was expectable.  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ , P, S,  $\text{Na}_2\text{O}$  and  $\text{MnO}$  with 8.70, 4.06, 1.89, 1.65, 0.6, 0.456 and 0.018%, respectively, were also found in the studied sludge. Comparing our results with those of Vieira et al.<sup>7</sup> from fine steel sludge showed that  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  in our studied sludge were lower, and  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  were higher than theirs.

### SWWTP Sludge disposal

Sludge quality requirements need considering sludge management methods, disposal and reuse practices.<sup>1</sup> In our study, a comparison of studied heavy metals with the standards determined by CSQG and FDEPSCTLs showed

that according to CSQG, Cu, Pb and Zn concentrations in the studied sludge were significantly beyond the permitted values for residential/ parkland, agricultural and commercial applications (see table 3). Cu and Zn concentrations are also significantly higher than CSQG standards for industrial applications. Table 3 also represents that compared to FDEPSCTLs, Fe and Zn concentrations in the studied steel sludge are significantly high for residential, and both residential and nonresidential applications, respectively, which restricts sludge's use for such applications.

### Land use

One of the methods for wastes managing is to use upper soil zone, which is defined as land use. Hazardous or toxic wastes are not advisable to use in this method. It is necessary to consider the amounts of pollutants in the sludge and the loading rate of a pollutant applying to the land to prevent their accumulation in the soil. Only sludge with pollutants within the recommended concentrations should be used on land. A relatively simple and cost effective method, land use uses natural processes for waste recycling and soil structure improving.<sup>17</sup>

In this study, as mentioned before, compared with CSQG standard for park land and agricultural use, Cu, Pb and Zn concentrations in the studied sludge were higher, which make it unsuitable for land application. There are researchers that have reported the exceeding of heavy metals in their studied sludge from

**Table 3. Statistical results of comparing the investigated heavy metals with the standards determined by CSQG and FDEPSCTLs**

Heavy metal	CSQG								FDEPSCTLs			
									soil direct exposure			
	Residential/ parkland		Agricultural		Commercial		Industrial		Residential		Non Residential	
	Standard (mg kg <sup>-1</sup> )	P*										
Al	-	-	-	-	-	-	-	-	80000	0.001 <sup>↓O</sup>	-	-
Cd	10	< 0.0001 <sup>↓W</sup>	1.4	0.234 <sup>↑W</sup>	22	< 0.0001 <sup>↓W</sup>	22	< 0.0001 <sup>↓W</sup>	82	< 0.0001 <sup>↓W</sup>	1700	< 0.0001 <sup>↓W</sup>
Cr	64	0.472 <sup>↓W</sup>	64	0.472 <sup>↓W</sup>	87	0.004 <sup>↓W</sup>	87	0.004 <sup>↓W</sup>	210	< 0.0001 <sup>↓W</sup>	470	< 0.0001 <sup>↓W</sup>
Cu	63	0.078 <sup>↑W</sup>	63	0.078 <sup>↑W</sup>	91	0.078 <sup>↑W</sup>	91	0.078 <sup>↑W</sup>	150	0.085 <sup>↓W</sup>	89000	< 0.0001 <sup>↓W</sup>
Fe	-	-	-	-	-	-	-	-	53000	< 0.0001 <sup>↑O</sup>	-	-
Mn	-	-	-	-	-	-	-	-	3500	< 0.0001 <sup>↓W</sup>	43000	< 0.0001 <sup>↓W</sup>
Ni	50	0.130 <sup>↓O</sup>	340	< 0.0001 <sup>↓O</sup>	35000	< 0.0001 <sup>↓O</sup>						
Pb	140	0.003 <sup>↑O</sup>	70	< 0.0001 <sup>↑O</sup>	260	0.083 <sup>↑O</sup>	600	0.011 <sup>↓O</sup>	400	0.926 <sup>↓O</sup>	1400	< 0.0001 <sup>↓O</sup>
Zn	200	< 0.0001 <sup>↑O</sup>	200	< 0.0001 <sup>↑O</sup>	360	< 0.0001 <sup>↑O</sup>	360	< 0.0001 <sup>↑O</sup>	440	< 0.0001 <sup>↑O</sup>	11000	< 0.0001 <sup>↑O</sup>

\* P-value < 0.05 is considered as a significant level.

↑ and ↓ indicate that measured amounts are higher and lower than standards, respectively.

O and W are p-values from One sample t-test and Wilcoxon signed rank test, respectively.

- shows that no standard value has been set.

CSQG: Canadian Soil Quality Guidelines

FDEPSCTLs: Department of Environmental Protection Soil Cleanup Target Levels

standards for land application.<sup>5</sup>

#### **Residential, commercial and Industrial uses**

Table 3 shows that Zn concentrations in the studied sludge were significantly higher than CSQG and FDEPCTLs for all types of applications. Cu and Pb both have restrictions to be used for residential and commercial uses. Cu also was significantly higher than CSQG for industrial uses. On the other hand, Fe concentration in the studied sludge was beyond the FDEPCTLs for residential applications. Some residential and non-residential applications of sludge have been discussed.

#### *Using as building and construction materials*

Incinerated sludge ash contains predominantly amount of Fe, Al, Ca and Si. Thus, it can be used as a raw material for manufacturing of construction materials such as bricks, tiles, blocks.<sup>18</sup> The results of XRF showed that these elements have the first to forth rank in the studied sludge. So that, studied sludge has a good potential for using as a raw material for manufacturing of construction materials. However, heavy metals content, which was above the standards, can restrict its application for this purpose. Although, according to FDEP guidance, sludge can be blend with uncontaminated soil to reduce the potential health threats from exposure to the sludge, provided that the resulting mixture be still appropriate for beneficial use. To determine the appropriate blend ratio (ratio of blend material to sludge) for lowering the contaminants contained in the sludge FDEP recommends the following equation:<sup>11</sup>

$$\text{Blend Ratio} = \frac{(A - B)}{(B - C)} \quad (1)$$

where,  $A$  = concentration of contaminant in the sludge, mg/kg,  $B$  = target concentration of the blended material, mg/kg,  $C$  = concentration of contaminant in the material used for blending, mg/kg.

In a similar study, Vieira et al., found that using 5 w.t% of the fine steel sludge is beneficial to the ceramic building. But, they did not

consider the heavy metal contents of the sludge.<sup>7</sup> In another study, Silva et al. used stabilized/solidification technology to treat sludge from an electroplating industry and the resultant product was used as a raw material to build concrete block. They found that the metal leachability and solubility of the resultant block is very low, indicating a low environmental impact.<sup>2</sup>

#### *Using in wastewater treatment*

Sludge can be used in waste water treatment process. For example, the leaching solution of a textile sludge incineration residue was studied for its coagulant effect on textile wastewater treatment. The results showed that it can be a coagulant agent for textile wastewater treatment.<sup>8</sup> Results of another study, revealed that pretreating the tannery sludge with a combination of tannery sludge incineration slag and cationic polyacrylamide can improve sludge dewaterability over cationic polyacrylamide conditioning alone.<sup>9</sup>

#### **Other uses of sludge**

As another reuse practice, pyrolysis process can be used to convert sludge with a high concentration of heavy metals or toxic chemicals to oil. The disadvantage of this method is its high capital and running costs.<sup>19</sup>

#### **Land filling**

The final option for disposal of the sludge that cannot be reused is their land filling. Since such sludge usually contain toxic materials, which can cause groundwater contamination, it is necessary to line the landfill with the proper lining materials, such as clay or plastic liner.<sup>19</sup>

Current management of the studied steel wastewater sludge is to discharge it, in the form of cake sludge, in an unlined dumping site. In such disposal method, sludge can contribute to landfill leachate, cause groundwater pollution, enter the food chain and cause health problem. Al Yaqout, recommended that lined evaporation ponds can be used as an economic and safe method for the industrial liquid and sludge disposal in arid climates.<sup>20</sup>

## Conclusion

In this study, different physicochemical characteristics, heavy metal contents and chemical composition of a steel wastewater treatment plant were investigated. The measured heavy metals compared with international standards and according to the obtained results compared with CSQG, the investigated sludge was polluted for residential/parkland, agricultural, commercial and industrial use because of its high Cu, Pb and Zn concentrations. It was also observed that according to FDEPCTLs, the studied sludge was not suitable for residential and non-residential applications due to its high Fe and Zn contents. It should also be mentioned that there are some other parameters, including different organic and inorganic compounds, in CSQG and FDEPCTLs than those investigated in this study and it would be better that these parameters be considered in future studies.

## Conflict of Interests

Authors have no conflict of interests.

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