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CONTINUOUS REMOVAL OF HEAVY METALS FROM FGD WASTEWATER IN A FLUIDISED BED WITHOUT SLUDGE GENERATION

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ABSTRACT

A patent pending fluid-bed process has been developed by Krüger for removal of dissolved heavy metals by adsorption/coprecipitation. The waste product is a very compact granulate with a very low water content of 10-20%. Sludge is not produced. The fluid-bed technique was tested at a coal-fired power station with wastewater from the flue gas desulphurisation (FGD) unit for removal of heavy metals from the wastewater. By dosing only potassium permanganate to the wastewater, the content of dissolved nickel, cadmium and zinc was reduced by respectively 99%, 92% and 97% at optimum treatment in one fluid-bed reactor. The weight of waste product produced will constitute less than 25% of the waste product produced by the present traditional chemical precipitation. Chemical costs are approximately 0.6 US$/m^3 which are similar for the fluid-bed and present wastewater treatment processes. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Adsorption; FGD wastewater; fluidised bed; heavy metals; manganese; waste reduction.

INTRODUCTION

Traditional treatment

Wet gypsum producing desulphurisation of flue gas from power plants produces a heavy metal-containing wastewater. At the Danish Avedøre Power Station this wastewater is treated by normal chemical precipitation. A diagram of the present treatment plant is shown in Figure 1. By dosing base, sulphide, iron and polymer to the wastewater followed by precipitation and separation, the content of dissolved heavy metals is lowered considerably as shown in Table 1. As seen, the present degree of treatment is very satisfactory; however, the amount of sludge produced and removed from the filter press constitutes approx. 2.0 kg/m^3 wastewater at optimum performance.

Owing to the increasing problems with disposal of sludge and costs for sludge disposal, Krüger A/S together with the Avedøre Power Station/ELKRAFT decided to investigate if Krüger's fluid-bed technique could be used for removal of heavy metals from the high ion-strength wastewater. In this way, a reduction of the volume/weight and increase of the handling of the waste product would be possible.

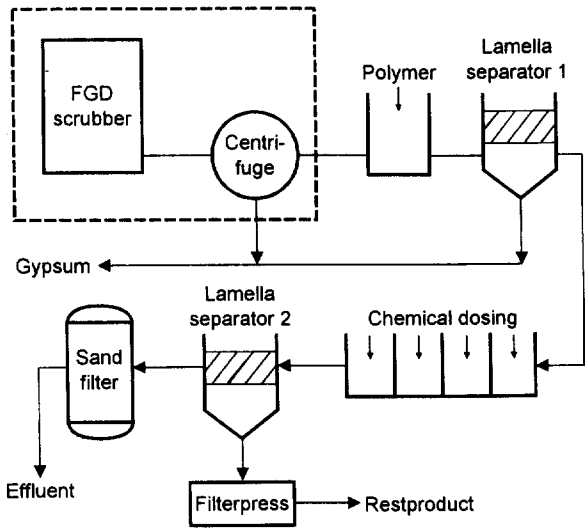

Figure 1. Present FGD wastewater treatment plant at Avedøre Power Station.

Table 1. Performance of traditional treatment at Avedøre Power Station

	Dissolved concentrations in wastewater		
	Untreated [μg/l]	Treated [μg/l]	Removed [%]
Ni	385	4.5	99
Cd	266	1.2	> 99
As	4.8	0.08	98
Hg	16	0.04	> 99

Krüger's fluid-bed technology

In recent years, Krüger has developed a fluid-bed technique for removal of dissolved heavy metals especially from groundwater and fly ash percolate, e.g. removal of chromate (Aktor, 1994), arsenic and nickel (Nielsen and Christemsen, 1996). A general description of the process is given below.

The fluid-bed treatment process is operated by continuous addition of manganous or ferrous ions and an oxidation agent (e.g. O_2, H_2O_2, $KMnO_4$) to the wastewater. Adding and mixing takes place in a fluid-bed reactor containing a carrier material. By controlling the process conditions, the oxidation of the manganous or ferrous ions will take place heterogeneously after adsorption onto the carrier material. An adsorptive granulate of either ferric oxyhydroxide or manganese dioxide will be generated as a coating on the surface of the carrier material. Hence, the adsorptive surface is continuously renewed and the added iron or manganese is removed. These processes have been investigated and described earlier by Janda and Benesová (1988) and Aktor (1993).

The overall heterogeneous oxidation of manganous ions with potassium permanganate can be illustrated as follows:

(1)

Manganese dioxide and ferric oxyhydroxide have significant adsorptive properties in relation to inorganic dissolved metals (e.g. Gadde and Laitinen, 1974; Benjamin *et al.*, 1982). The metals coprecipitate/adsorb to the granulate in the fluid-bed reactor and are built into the constantly increasing manganese dioxide or ferric oxyhydroxide coating.

Compared to conventional chemical treatment with sludge production the compact granulate waste product has excellent handling properties; the density of the granulate is 2-3 kg/l. Furthermore, the waste stream is reduced significantly because the coating has a very low water content (10-20%).

Adsorption/coprecipitation of metals in FGD wastewater

Adsorption/coprecipitation of dissolved heavy metals depends on some important parameters such as pH, adsorbent concentration, competing adsorbates and complexing ligands (Benjamin *et al.*, 1982).

The FGD wastewater from the Avedøre Power Station contains high concentrations of especially calcium (9 g/l), magnesium (2 g/l), chloride (25 g/l) and sulphate (1 g/l). These ions will compete with the heavy metals for the adsorption sites and in this way reduce the removal efficiency. Further, mercury forms complexes with chloride ions which decrease the adsorption/coprecipitation of mercury (Inoue and Munemori, 1979).

Manganous ions are not oxidised in the FGD scrubber contrary to ferrous ions. Hence, the wastewater contains 40-100 mg/l Mn(II) which can be utilised as a reducing agent in the fluid-bed process, thereby reducing the chemical costs. However, whether manganese dioxide or ferric oxyhydroxide would be the most effective adsorbent generally for the different heavy metals was not known prior to these experiments. According to theory, manganese dioxide is the best adsorbent for cations and ferric oxyhydroxide is most effective for removal of anions.

It is known from theory and other pilot plant tests that controlling pH can increase the adsorption/coprecipitation significantly. Theoretically, a decrease in pH increases the removal of anions but decreases the removal of cations. Natural pH of the FGD wastewater is in the range from 6.5 to 7.5.

METHODS

Prior to the investigations presented in this paper treatment of industrial wastewater by the fluid-bed process had not been performed. So, to investigate the effect of the above parameters several batch tests had to be performed with FGD wastewater from the Avedøre Power Station before pilot plant fluid-bed tests could be started.

The investigation was divided into 3 phases:

1) Characterisation of FGD wastewater.

2) Batch experiments with FGD wastewater (batch experiments will not be described in detail in this paper).

3) Pilot plant fluid-bed experiments at the Aved_re Power Station.

A diagram of the experimental set-up for the pilot-plant experiments is shown in Figure 2.

A fluid-bed reactor with an inner diameter of 0.145 m and a height of 5.5 m was used. The reactor was operated at filter velocities ranging from 14 to 30 m/h. The filter material was quartz sand.

FGD wastewater taken from after lamella separator 1 was added to a 1.5 m^3 buffer tank and from that introduced into the bottom of the fluid-bed reactor; here, it was mixed with recirculated treated water and a potassium permanganate solution. To control pH sodium hydroxide could be added too.

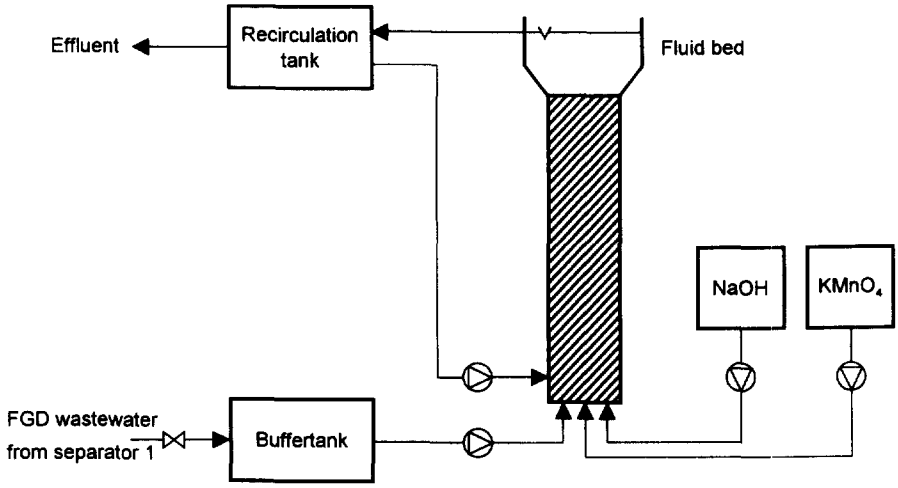

Figure 2. Schematic drawing of the fluid-bed pilot plant

Samples for heavy metals and manganese were taken from the buffer tank and the recirculation tank after a minimum of 24 hours' steady-state operation. After sampling, the wastewater was preserved with acid and stored at 5°C until analysis. For analyses of dissolved compounds the wastewater was 0.45 µm filtered before preservation. Analyses for nickel and cadmium were done by atomic absorption spectrophotometry equipped with graphite furnace (AAS-GF). Zinc and manganese were determined by AAS and arsenic was determined by AAS with hydride technique. Analyses for mercury were not performed due to batch test results - see below. Samples for pH were taken at the bottom of the fluid-bed reactor.

RESULTS AND DISCUSSION

Characterisation of the wastewater showed that the heavy metals were only in dissolved form after lamella separator 1. Hence, it was decided that wastewater to the batch and fluid-bed experiments should be taken from the effluent from separator 1.

The results from the batch experiments showed that the best adsorption/coprecipitation was seen by using manganese dioxide as adsorbent. Oxidation of the natural content of manganese(II) in the wastewater by potassium permanganate gave a sufficient production of adsorbent for a removal of e.g. Ni, Cd, As and Se above 85-98%, despite the high ion-strength of the wastewater. However, the removal of mercury was below 25% in all experiments, so as could be expected, complex formation with chloride decreased the adsorption/coprecipitation significantly.

In the light of the above results pilot plant tests were started.

Chosen results from the pilot plant experiments are shown in Table 2. The filter velocity, the wastewater flow and pH were varied as indicated.

Table 2. Results of pilot plant treatment of FGD wastewater

Filter velocity [m/h]	30	23	19	17	14
Wastewater flow [l/h]	72	55	36	32	29
pH	8.4	8.4	8.8	7.2	8.4
		Manganese			
$Removed_{total}$ [%]	71	81	82	90	89
$Removed_{dissolved}$ [%]	99.7	99.9	99.9	99.8	99.7
		Nickel			
$Dissolved_{influent}$ [μg/l]	730	800	640	510	510
$Dissolved_{effluent}$ [μg/l]	21	10	2	7	3
Removed [%]	97.1	98.8	99.7	98.6	99.4
		Cadmium			
$Dissolved_{influent}$ [μg/l]	680	800	730	640	640
$Dissolved_{effluent}$ [μg/l]	140	67	20	53	27
Removed [%]	79.4	91.6	97.3	91.7	95.8
		Zinc			
$Dissolved_{influent}$ [μg/l]	2000	1800	1600	1900	1900
$Dissolved_{effluent}$ [μg/l]	320	250	200	50	75
Removed [%]	84.0	86.1	87.5	97.4	96.1
		Arsenic			
$Dissolved_{influent}$ [μg/l]	2.9	3.1	2.6	2.9	2.9
$Dissolved_{effluent}$ [μg/l]	1.7	2.8	2.3	1.3	2.2
Removed [%]	41	10	12	55	24

The content of total and dissolved heavy metals in the influent and effluent was identical

The pilot plant results show generally that a very satisfactory treatment for especially nickel, cadmium and zinc can be achieved by adsorption/coprecipitation onto manganese dioxide in the fluid-bed reactor. Nickel, cadmium and mercury are regarded as the most polluting metals in the wastewater.

Decreasing the filter velocity from 30 m/h to 14 m/h with a constant pH of 8.4 increases the removal of all metals except arsenic. However, the influent concentration of arsenic is very low and removal of arsenic is not essential according to discharge standards.

Increasing pH from 7.2 (original wastewater pH) to 8.8 at filter velocities of 14 to 19 m/h gives only a minor increase of the removal of nickel and cadmium but decreases the removal of zinc, arsenic and total-manganese. Hence, an adjustment of pH has not been shown to be cost-effective.

Table 3 compares the treatment of FGD wastewater by traditional precipitation and filtration with the fluid-bed filtration in a single column without pH adjustment. The amount of waste product produced by fluid-bed filtration is calculated to be less than 25% weight and 20% volume than the waste product produced by optimum traditional treatment. Chemical costs will be very similar.

The removal of heavy metals is less efficient in the investigated fluid-bed pilot plant. However, if necessary, two fluid-bed columns can be connected in series and in that way increase the removal significantly. By bypassing FGD wastewater with manganese(II) directly to the second column the production of waste product and chemical costs will not increase compared to the level shown in Table 3.

As mercury is not removed by adsorption/coprecipitation it has to be removed by other means than fluid-bed filtration.

Table 3. Comparison of treatment methods

	Traditional treatment			Fluid-bed treatment		
	Influent [μg/l]	Effluent [μg/l]	Removed [%]	Influent [μg/l]	Effluent [μg/l]	Removed [%]
Nickel	385	4.5	98.8	510	7	98.6
Cadmium	266	1.2	99.5	640	53	91.7
Arsenic	4.8	0.08	98.3	2.9	1.3	55.2
Waste product* [kg/m^3]		2.0			0.5	
Waste product* [l/m^3]		1.8			0.3	
Chemical costs* [US$/m^3]		~ 0.5			~ 0.6	

* fluid-bed treatment: including additional treatment for mercury

Based on these good results from pilot plant fluid-bed testing, the construction of a demonstration plant is taking place in 1997. A full-scale fluid-bed treatment plant will be more compact and simple to operate than a traditional plant and the capital costs will be lower.

CONCLUSIONS

Pilot plant experiments at a Danish coal-fired power station with wastewater from the gypsum producing flue gas desulphurisation unit have shown that a new developed fluid-bed technique for removal of dissolved heavy metals can be used for treatment of the high ion-strength FGD-wastewater. By dosing only potassium permanganate to the wastewater in one fluid-bed reactor a removal of nickel, cadmium and zinc of 99%, 92% and 97% respectively can be obtained. Removal of other heavy metals such as arsenic and selenium will also occur. A significant removal of mercury cannot be expected due to complex formation with chloride.

The waste product from the fluid-bed treatment is a compact granulate with a density of 2.5-3.0 kg/l and after manual dewatering the water content is below 20%. Compared to the sludge waste product, produced by traditional chemical precipitation, the weight and volume of the waste product constitute less than 25%. The chemical costs for the fluid-bed treatment will be approximately 0.6 US$/m^3, which is similar to the costs for the present traditional treatment. A full-scale fluid-bed plant will be very compact and the continuous operation will be simple.

The fluid-bed technique has been shown to be capable of treating industrial wastewater and groundwater for several dissolved heavy metals such as Cd, Ni, Zn, Cr, Se and As, and removal of other metals is currently being tested.

ACKNOWLEDGEMENT

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REFERENCES

Aktor, H. (1993). Ultra high-rate removal of ferrous iron by fluid-bed filtration. *European Water Filtration Congress*, March 1993, Oostende, Conf. Proc., 1.23-1.30.

Aktor, H. (1994). Continuous high-rate removal of chromate in a fluidised bed without sludge generation. *Wat. Sci. Tech.*, **30**(7), 31-40.

Benjamin, M. M., Hayes, K. F. and Leckie, J. O. (1982). Removal of toxic metals from power-generation waste streams by adsorption and coprecipitation. *Journal WPCF*, **54**(11), 1472-1481.

Gadde, R. R. and Laitinen, H. A. (1974). Studies of heavy metal adsorption by hydrous iron and manganese oxides. *Analytical Chemistry*, **46**(13), 2022-2026.

Inoue, Y. and Munemori, M. (1979). Coprecipitation of mercury(II) with iron hydroxide. *Env. Sci. Tech.*, **13**(4).

Janda, V. and Benesová, L. (1988). Removal of manganese from water in fluidized bed. *Aqua*, **6**, 313-315.

Nielsen, P. B. and Christensen, T. C. (1996). Continuous high-rate removal of nickel and arsenic in a fluid- bed reactor. *IWSA workshop. Natural origin inorganic micropollutants: arsenic and other constituents*, May 1996, Vienna, Preprints, 129-137.