EFFECT OF POLARIZATION ON MANGANESE BIOFOULING OF HEAT EXCHANGER SURFACES

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ABSTRACT

We investigated biofouling of titanium (Ti) and stainless steel (SS) lamellar heat exchangers operating on Baltic seawater. Potential of polarization for anti-fouling was studied with pilot scale heat exchanger connected to side flow of an industrially operating heat exchanger.

The deposits were characterized by Field Emission Scanning Electron Microscopy (FESEM), Scanning Electron Microscopy Energy Dispersive X-ray (SEM-EDX) and by chemical and biological analytical methods. The deposits contained high concentration of manganese and micro-organisms with formation that looked like Mn-nodules. The manganese could not be removed from the surface of industrially operating lamellar heat exchanger by pressure wash cleaning. Results revealed that dominantly cathodic pulsed polarization inhibited and dominantly anodic pulsed polarization promoted Mn fouling compared to non-polarized surfaces.

Microbial identification based on 16S rRNA gene sequence showed that *Shewanella* species were dominating in deposits among culturable aerobic and microaerophilic taxa. *Pseudomonas, Flavobacterium* and *Aeromonas* were also found and they belong to manganese accumulating genera.

INTRODUCTION

Wet industrial processes provide an environment for formation of microbial and chemical deposits. Biofouling on process surfaces cause equipment dysfunction, contamination, corrosion and loss of energy transfer (Sly et al., 1990; Heal et al., 1995; Dickinson and Lewandowski, 1996). Previous researches have shown accumulated deposits in drinking water distribution systems contain manganese concentrated from water and have revealed the role of bacteria on manganese oxidation and manganese attachment on surface (Sly et al., 1990; Mandernack et al., 1995; Murdoch and Smith, 1999; Emerson, 2000; Kielemoes et. al., 2002). In addition, the presence of the Mn-nodules like particles is dependent on the presence of bacteria capable of oxidizing manganese (Murdoch and Smith, 1999).

In heat exchanger environment deposits have been considered mainly inorganic not biological. Pressure wash cleaning and chlorination have been used as anti-fouling treatments in order to control fouling on the surface of heat exchanger (Sly et al., 1990; Sriyutha Murthy et al., 2003). Our study showed that manganese containing deposits could not be removed by pressure wash cleaning.

In order to control the accumulation and to investigate the effect of anti-fouling treatment (polarization) on fouling, we constructed unique pilot scale heat exchanger operating on Baltic seawater.

MATERIALS AND METHODS

Field Emission Scanning Electron Microscopy (FESEM) images were obtained using Hitachi S-4800. Scanning Electron Microscopy Energy Dispersive X-ray (SEM-EDX) analysis were performed using JEOL JSM-840A Röntec Edwin Winshell instruments. Ti-coupons from pilot scale heat exchanger were rinsed with sterile tap water, fixed in 3% glutaraldehyde in Sörensen phosphate buffer (pH 7) for 3-5h, dehydrated in a series of 50-100% of ethanol (4 steps) and critical point dried. Before FESEM-analysis Ti-coupons were Cr coated. Deposits from titanium lamellar heat exchanger were air-dried and gold coated before SEM-EDX-analysis.

Metal analysis from seawater and heat exchanger deposits were performed using ICP-MS and Flame-AAS instruments. Ash, dried weight and organic matter from heat exchanger deposits were analyzed using ISO 6245 method. Total culturable bacteria count was done on R2A plates prepared in Baltic seawater. For microaerophilic count, plates were incubated 11d at 12 ºC in microaerophilic environment. The microbial identification based on 16S rRNA gene sequence.

Polarization experiments were carried out using pilot scale heat exchanger (built by Savcor Company, Mikkeli, Finland) connected to side flow of an industrially operating heat exchanger (Figs. 1 and 2). Pilot scale heat exchanger contained 10 titanium test coupons (10mm*40mm each), allowing simultaneous exposure of the coupons to 4 different polarization treatments (2 parallels each, 1 reference pair). Power was fed with wire electrodes. The potential of each Ti-coupon pair was measured against Ag/AgCl-reference-electrode. Polarizations were pulsed direct current following AP1 and CP1 polarization programs (designed by Savcor Oy, Mikkeli, Finland, www.savcor.com). The chosen polarization potentials were below the potential that would corrode Ti.

The pilot scale heat exchanger was fed with the water of industrial scale heat exchanger (seawater flow 2.0 l/min and temperature 15-28 ºC).

Pressure wash of the lamellar heat exchanger was executed using fresh water and 140-160 bars. The washing interval of the plates was 2 months.

RESULTS

Ti-coupons exposed for 2 weeks to Baltic seawater in side flow of industrially operating heat exchanger were intensively populated by Mn-nodule like particles (Fig. 3). The deposits from industrial scale lamellar heat exchanger contained high concentration of manganese and micro-organisms (Table 1). Manganese persisted after 140-160 bars pressure wash (Fig. 4-5) and the concentration of manganese in the persisting deposits after cleaning was up to 30% of dry weight (Table 1). In contrast iron was not enriched by pressure wash. Manganese and iron are minor elements in Baltic seawater (110 µg/l and 650 µg/l, Table 2).

In 2 weeks non-polarized Ti-coupons used in the pilot scale heat exchanger had accumulated mainly Mn-nodule deposits (Table 3). SEM-EDX-analysis from the Ti-coupons revealed that dominantly cathodic pulsed polarization inhibited and dominantly anodic pulsed polarization promoted Mn fouling compared to non-polarized surfaces.

Shewanella species were dominating in heat exchangers deposits among the culturable aerobic and microaerophilic taxa. Deposits were also found to contain *Pseudomonas, Flavobacterium* and *Aeromonas species.*

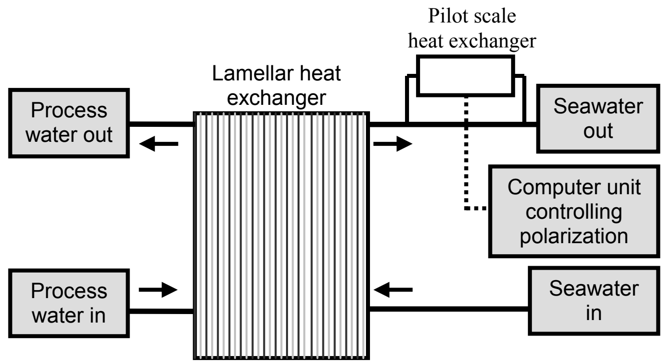


Fig. 1. Process scheme of the pilot and industrial scale heat exchanger.

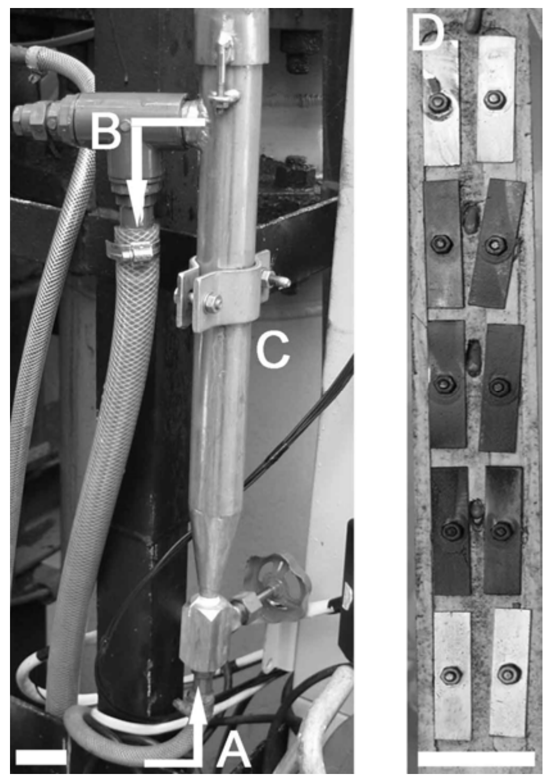


Fig. 2. The figure shows the pilot scale heat exchanger connected to side flow of an industrially operating heat exchanger. (A) seawater intake, (B) seawater exhaust, (C) cylinder for the titanium test coupons and (D) Ti-coupons after 2 weeks of exposure to Baltic seawater. Seawater flow 2.0 l/min and temperature 15-28 ºC. Bars denote 4 cm.

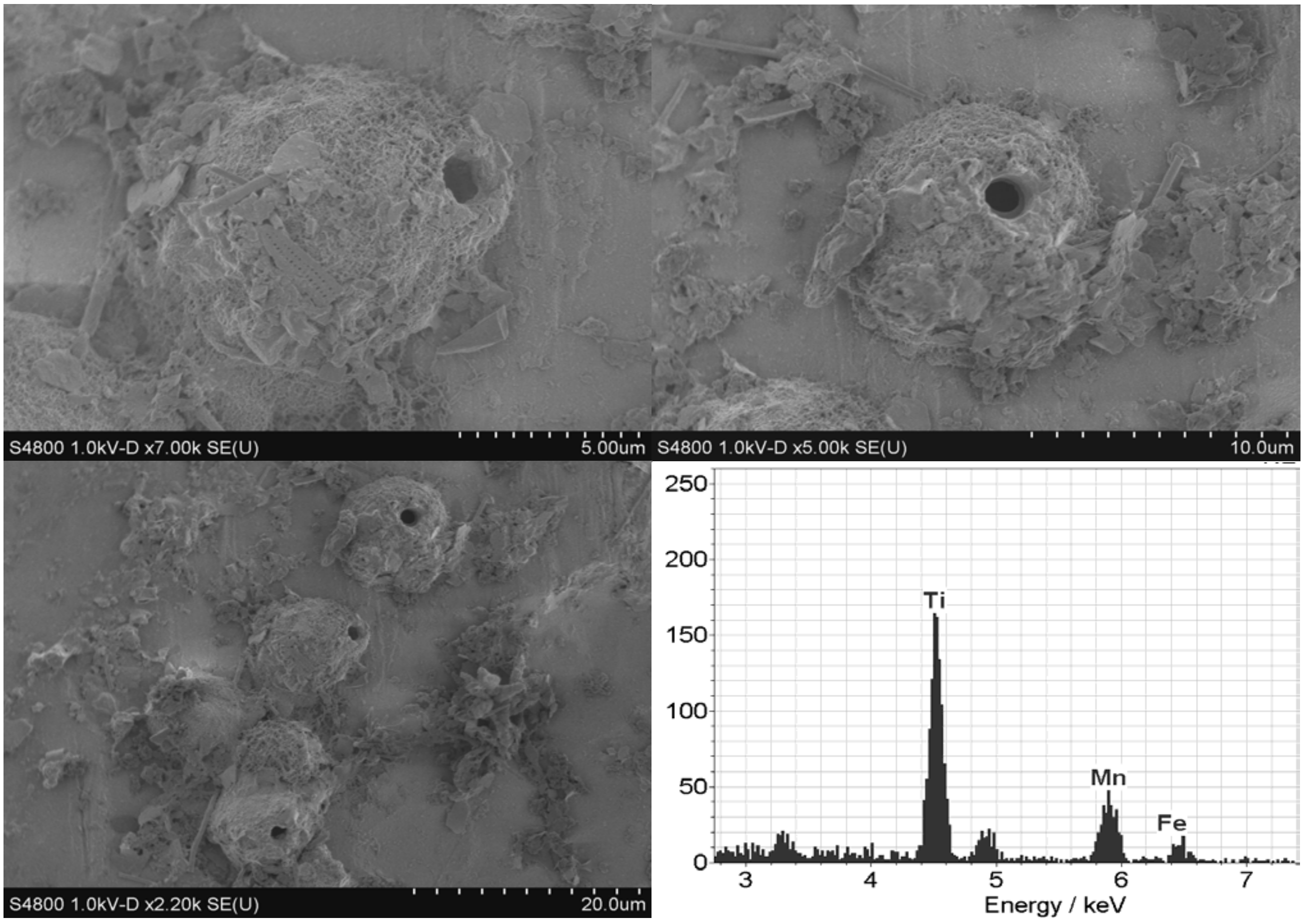


Fig. 3. FESEM micrographs and EDX-analysis of Ti-coupons from the pilot scale heat exchanger. The coupons after 2 weeks of exposure to Baltic seawater connected to side flow of industrially operating heat exchanger. EDX-analysis was made from the nodule shown in FESEM micrograph. Ti-coupons were fixed with glutaraldehyde, dehydrated with ethanol, critical point dried and Cr coated before FESEM-analysis.

Table 1. Chemical and biological composition of the deposits on the surface of industrial scale lamellar heat exchanger operating on Baltic seawater. Colony forming units per gram wet weight (cfu g^{-1}) cultivated under microaerophilic and aerobic conditions and bacteria identified. Heat exchangers were made of stainless steel (SS) and titanium (Ti). Deposits were collected 2 months after previous pressure wash (pressure 140-160 bars).

	Dry weight	**% of dry weight**				**Micro-aerophilic**	**Aerobic**	**Bacteria identified** (known Mn depositing underlined)
		Org. matter	**Ash**	**Mn**	**Fe**	**cfu g^{-1} wet weight**		
Before pressure wash (SS)	11.5	23.4	9.3	1.6	9.6	$8.3*10^7$	$2.3*10^9$	*Shewanella sp.*, *Pseudomonas sp.*, *Shewanella massilia*, *Shewanella baltica*, *Aeromonas sp*, *Flavobacterium sp.*, *Shewanella putrefaciens*
After pressure wash (SS)	26.6	19.1	21.0	30.1	3.5	$5.3*10^7$	$2.1*10^8$	
Before pressure wash (Ti)	12.9	19.3	9.8	1.6	7.8	$2.8*10^8$		
After pressure wash (Ti)	16.4	21.6	12.8	17.1	6.1	$3.0*10^8$	$2.1*10^9$	

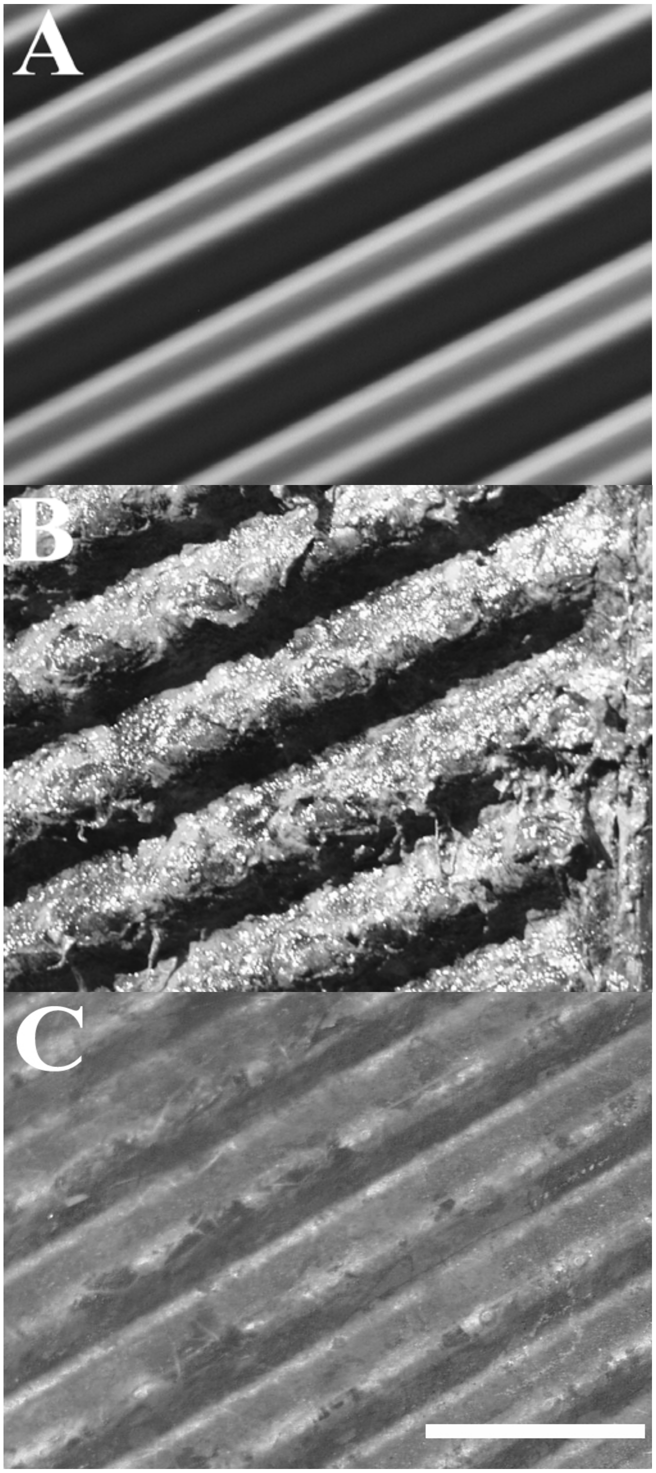


Fig. 4. Surface of the industrial scale lamellar heat exchanger made of Ti (A) unused, (B) before the pressure wash and (C) after the pressure wash. The washing interval was 2 months and pressure used was 140-160 bars. Bar denotes 3 cm.

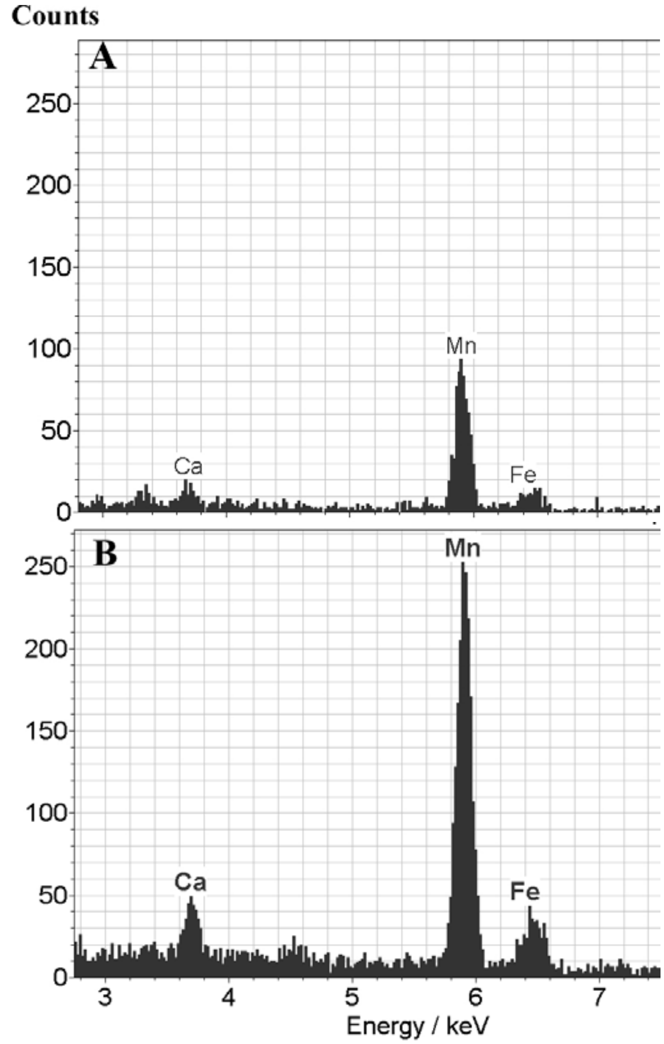
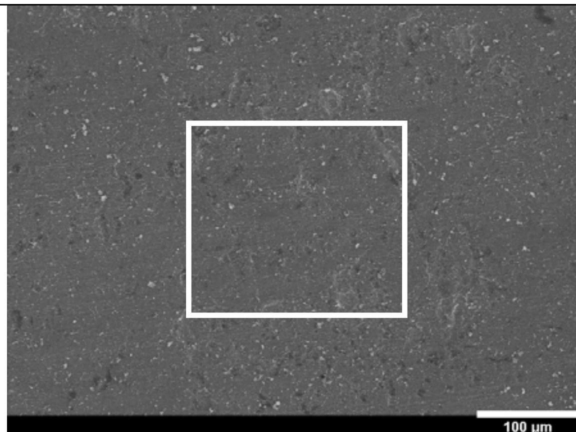
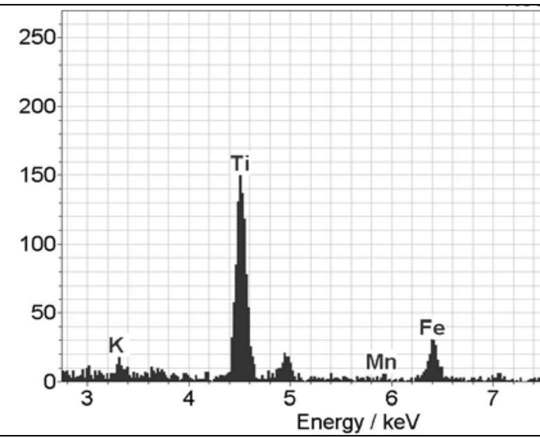


Fig. 5. EDX-analysis from the deposits accumulated on the industrial scale Ti-lamellar heat exchanger surface (A) before and (B) after the pressure wash. The washing interval was 2 months.

Table 2. Concentration of Mn and Fe in Baltic seawater.

Element	Concentration (µg/l)
Mn	110
Fe	650

Table 3. SEM micrographs and EDX-analysis of Ti-coupons from the pilot scale heat exchanger. The coupons after 2 weeks of exposure to Baltic seawater connected to side flow of industrially operating heat exchanger. Loci of the performed EDX-analysis are shown by box. Ti-coupons were fixed with glutaraldehyde, dehydrated with ethanol and critical point dried before analysis. Mn-nodule like particles were seen on non-polarized and anodically polarized Ti-coupons. Anodically polarized coupons were covered with Mn-deposits, both nodules and other forms. Cathodically polarized coupons accumulated no significant Mn. Bar denotes 100 µm.

<table>
<tr><th>Anti-fouling treatment</th><th>SEM image</th><th>EDX-analysis</th></tr>
<tr><td>Dominantly cathodic pulsed polarization (CP1)</td><td>
</td><td>
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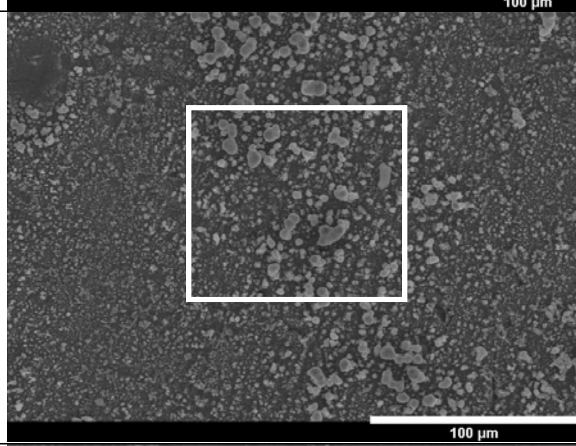
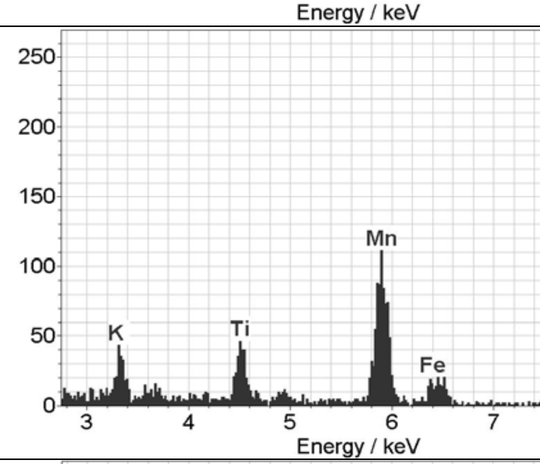
<tr><td>Dominantly anodic pulsed polarization (AP1)</td><td>
</td><td>
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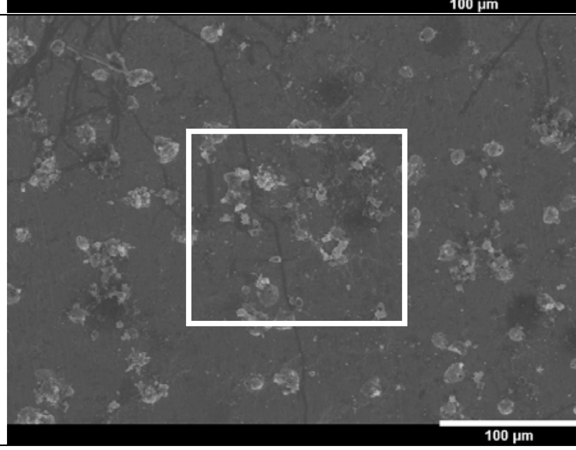
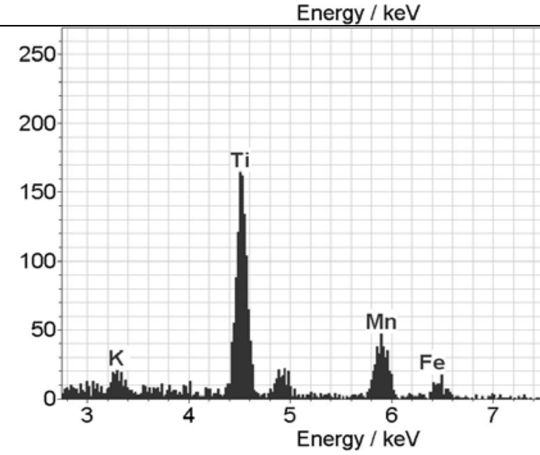
<tr><td>No anti-fouling treatment</td><td>
</td><td>
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DISCUSSION

Our investigations revealed the accumulation of Mn-nodules on the surfaces of pilot scale lamellar heat exchanger connected to side flow of an industrially operating heat exchanger. Murdoch et al. (1999) had observed similar looking Mn containing nodules in their studies of water pipeline materials inoculated with *Pseudomonas spp*. After 2 weeks Mn-nodules they found looked the same as we discovered and nodules were approximately 10 µm diameters and had a central opening of 2 µm. *Pseudomonas, Flavobacterium* and *Aeromonas species* found in our study are known for being capable of accumulating manganese from seawater by oxidizing soluble Mn^{2+} to insoluble MnO_2 (Ehrlich et al., 2002). Mn^{2+} is the most common form of Mn in seawater whereas MnO_2 is relatively rare, insoluble at pH ~7 and attaches very firmly to surfaces.

Our study showed Mn containing deposits are major problem in heat exchangers operating on Baltic seawater. Ti-coupons exposed to Baltic seawater revealed Mn-nodules attaching first to the surface. In addition, Mn remained on the surface of industrial scale lamellar heat exchanger after 140-160 bars pressure wash whereas other deposits were removed. Using pressure higher than 160 bars for wash is not possible because it will break the insulating tape used between adjacent lamellar heat exchanger plates. This study shows polarization is good alternative to combined with pressure wash. Dominantly cathodic pulsed polarization prevented Mn accumulation.

CONCLUSIONS

1. The deposits on the lamellar heat exchanger contained manganese 1000000 times higher concentration compared to the Baltic seawater used as the fluid.
2. SEM-EDX-analysis revealed that Mn containing deposits persisted pressure wash.
3. Mn-nodule like deposits accumulated on Ti-coupons exposed to Baltic seawater in pilot scale heat exchanger.
4. Some of the bacteria identified from the deposits belong to known Mn accumulating genera.
5. Dominantly cathodic pulsed polarization inhibited Mn accumulation.

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