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# Atmospheric corrosion due to amine emissions from carbon capture plants

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### ABSTRACT

The atmospheric corrosion due to pure amines emitted from carbon capture plants was investigated. Amine exposure was found to initially inhibit the corrosion of steel, by its film formation and alkalinity, but reduce corrosion product layers and lead to freezing point depression, which could in turn increase the corrosion. Very high amine doses were observed to dissolve the metal without the establishing of a corrosion layer. These effects seem much more pronounced on copper than on steel. Climate and air quality variations affect the steel corrosion much more than the expected maximum amine deposition from carbon capture plant emissions.

### 1. Introduction

There is a strong interest in carbon capture and storage (CCS) to mitigate climate change. This is seen as a necessary technology to reduce the CO<sub>2</sub> emissions to the atmosphere from the burning of hydrocarbons (Shao and Stangeland, 2009). One promising technology for this purpose is the absorption of CO<sub>2</sub> from flue gases by amines. Some amount of the amines and of their degradation products are known to escape to the atmosphere during this process. It is a demand from environmental authorities to document the risks to health and the environment from industrial emissions. The aim of the investigations described in this paper was to supply such documentation about possible corrosion effects on infrastructure of released amines from CCS plants.

The operation principle of carbon capture by amines is, basically, that the flue gas rises through an absorption tower in a spray of falling amine solution, which chemically bonds with the CO2 to a carbamate salt, before the cleaned (stripped) exhaust escapes to the atmosphere. The amines associate with high pH and low conductivity and are generally not themselves corrosive but may become so when they absorb CO<sub>2</sub> or H<sub>2</sub>S (Kittel and Gonzalez, 2014). The amine is both oxidatively and thermally degraded in this process to produce a range of waste products, including ammonia, amides, aldehydes, volatile acids, nitrosamines, and nitramines (SEPA, Scottish Environment Protection Agency, 2015). The carbamate salts are part of a potentially very corrosive inside reformer environment (Kittel and Gonzalez, 2014; Botheju, 2006). One commonly used amine is mono-ethanolamine (MEA). With increasing concentrations of MEA the corrosion rate of the system has been reported to increase sharply (Kittel and Gonzalez, 2014), as the total amount of  $CO_2$  absorbed into the amine solution increases resulting in higher amounts of reducible bicarbonate (HCO<sub>3</sub>) and hydronium (H<sub>3</sub>O<sup>+</sup>) ions (Kladkaewa et al., 2011). The corrosion contributes to the formation of additional waste products.

Carbon capture by amines was tested in the so-called Technology Test Centre Mongstad on the western coast of Norway from the beginning of the 2010s. In a "design" scenario from the Aker Clean Carbon (ACC) technology CO<sub>2</sub> capture plant using the reported flue gas emissions from the CHP (Combined Heat and Power plant), the maximum expected direct emission of MEA to the air was quantified to 0.04 g/s, dispersing to a modelled maximum deposition of 1.6  $mg/m^2$  year to the ground. This represented a maximum mean hourly air concentration of 2  $\mu$ g/m<sup>3</sup> MEA as compared to 10  $\mu$ g/m<sup>3</sup> of ammonia (Berglen et al., 2010). Later measurements of the flue gas-streams from the carbon capture with MEA in this plant, in 2015, showed a solvent loss calculated as pure MEA of 1.6  $\pm$  0.1 kg/ton CO<sub>2</sub> captured. Ammonia emission was 67% of the loss. Other identified degradation products made up 16% of the loss. The MEA and alkyl amine emissions were found to be in the parts per billion ranges and nitrosamines and nitramines were below detectable levels (Morken et al., 2017). The amines and amine degradation products that are released to the atmosphere undergo dispersion and complex chemical reactions in the gas, aqueous (aerosols, cloud droplets, fog, and rain) and particle (aerosol) phases (SEPA, Scottish Environment Protection Agency, 2015). The oxidation of ammonia in the atmosphere is slow and its removal is mainly due to wet and dry deposition, partly after reaction with acidic components (sulfuric, nitric, and hydrochloric acids) to form ammonium salt aerosols (Renard et al., 2004). The main products of the atmospheric degradation of amines are different amides, but a number of aldehydes, nitrosamines and nitramines will also be formed (Bråten et al., 2008; Knudsen et al., 2009).

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Suspected toxic effects of the nitrosamines and nitramines and the determination of tolerable health exposure limits has been a major concern (SEPA, Scottish Environment Protection Agency, 2015).

As the pure amines seem under ordinary operation only to be a minor fraction of the emissions to air, it is essential to understand the atmospheric corrosion potential of the degradation products, which may have a different chemistry and impact than the pure amines. Ammonia and ammonium hydroxide are not particularly corrosive in themselves and are not usually included among the agents of outdoor atmospheric corrosion which needs consideration (Graedel and Leygraf, 2000). Corrosion problems can arise with specific materials, particularly when (other) contaminants are present. For example, with copper, ammonia typically react to form an intensely blue copper/ammonium complex (Davies, 2006). The formation of corrosive ammonium salt aerosols, such as ammonium chloride (NH<sub>4</sub>Cl) and ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) (Renner and Wolke, 2008), does not represent a net increase in corrosive compounds. Due to the observed domination of ammonia in the amine related emissions from carbon capture it may well be that any possible atmospheric corrosion due to regular plant emissions, or due to possible accidental releases, would be mostly ammonia corrosion of particularly sensitive materials, such as copper, in combined reaction with other atmospheric pollutants and the surface wetness. Organic nitrates can be generated during the complex atmospheric degradation of the amines (Bråten et al., 2008). The potential exists for nitrate in precipitation to be involved in the corrosion of iron. Ferric nitrate has been found on corroded iron. Only at very high nitrate concentrations is it expected that copper corrosion will contain nitrate (Graedel and Leygraf, 2000).

This work investigated the effect of the pure amine MEA, and partly of two other well documented amines used for carbon capture, diethanolamine (DEA) and 2-amino-2-methyl-1-propanol (AMP), on the atmospheric corrosion of carbon steel and copper. Carbon steel is a standard material used to assess corrosion rates and ISO corrosion classes. Copper is known to react with ammonia, and it was suspected that it might be corroded by the chemically related amine compounds. The possible corrosion effects of the amine degradation products were not investigated. Different amines have been reported to inhibit corrosion of carbon steel by neutralizing and film formation in acidic solution (Chen and Yang, 2019). As the metal surface coverage by the inhibitor molecules is essential for the effect of an inhibitor the concentration of the inhibitor is critical (Dariva and Galio, 2014). Testing of MEA as a corrosion inhibitor for steel in concrete, and the in-mixing of the closely related compound N,N'-dimethylethanolamine (DMEA) in commercial corrosion inhibitors for this purpose, has been reported (Myrdal, 2010). However, no data were found about outdoor atmospheric corrosion effects of exposure to MEA, DEA or AMP. The investigations in this work were performed by applying the amines to experimental samples of the metals in clean and polluted atmospheres in controlled climate situations in the laboratory and outdoors at field test stations with different types of atmospheres, which were measured along with the material exposures. The experiments were performed in 2011 and 2012. The results could be published in 2021.

### 2. Materials and methods

Metal plate samples of standard size were exposed in the laboratory and at the outdoor field test stations with regular spraying or brushing (at only one outdoor station) of amine solutions, or pure de-ionised water to control samples. The laboratory tests allowed exposures in controlled climates with the possibility for the addition of single air pollutants, and the exposure to higher amine doses by more frequent solution spraying than was possible in the field. The field tests on the other hand allowed exposures that more realistically simulated the outdoor situation after possible amine releases from plants. Controlled atmospheric corrosion exposures in the laboratory are recommended to study mechanisms and effects of pollutants but are typically not found to replicate ambient outdoor exposures (Graedel and Leygraf, 2000). Outdoor exposures are therefore needed to determine "real-life" dose-response effects (Kucera et al., 2007; Tidblad et al., 2017).

The DC 01 cold rolled low carbon steel (Fe) samples had dimensions  $15 \times 10 \times 0.1$  cm and a reported elemental content of C = 0.05 %, Mn = 0.20%, P = 0.01\%, S = 0.01\%, = 0.003%, Al = 0.04%. The production of, and possible trace elements in, the (acquired as) pure copper samples, obtained from the author's institute assortment in storage, were not specified. Although this may limit the possibility for inter-comparison with other copper corrosion studies, the results should provide a valid comparison to the carbon steel in this study. All the steel samples exposed outdoors and most of the steel samples exposed in the laboratory were from a Swedish retailer. Towards the end of the laboratory experiments the Swedish samples were finished, and the last laboratory experiments were performed with DC01 steel samples of the same dimensions from an earlier batch from a Norwegian retailer. A record of the trace elements in this batch was unfortunately not available. There is an, undetermined, uncertainty in the comparison of the results for these and the earlier (Swedish) samples. All the samples were degreased with a commercial degreasing agent (Simple Green®), rinsed with warm water and acetone, fan dried in the laboratory, wrapped in drying paper, and transported in paper envelopes in dry conditions to the mounting location. The exposure doses of the amine solutions were calculated from the reported value of the maximum expected deposition of MEA (1.6  $mg/m^2$  year), to represent a number of years of exposure on the ground to MEA (u = 61.1), DEA (u = 105.16) or AMP (u = 89.16) near the emission source.

### 2.1. Laboratory test

The accelerated laboratory tests were performed by exposing steel samples, and a few copper samples, to concentrations of  $6.5 \times 10^{-4}$  M or  $6.\ 5\times 10^{-2}\ \text{M}$  of the selected amines. The exposures were made in two different exposure chambers, a stable climate and pollution chamber (Fig. 1A) and a fog chamber (Fig. 1B). In the stable climate and pollution chamber the samples were discontinuously sprayed with the amines, to periodically dry between the spraying, as in the outdoors experiments. Sulphur dioxide (SO<sub>2</sub>) was added to the chamber air in some of the experiments. In the fog chamber the samples were exposed to a continuous amine aerosol and water droplet fog that was thought to, possibly, be more representative for an ambient exposure situation with precipitation wetting. Although the applied amine doses in the two experimental regimes could not be directly and quantitatively compared, they were supposed to, together, provide more information and results (statistics) about the direction and amount of the amine doseeffects.

The stable climate and pollution chamber consisted of three separate smaller chambers with volumes of 10 l immersed in a constant temperature water bath. The metal samples hung from a horizontal metal rod crossing the top centre of the chambers. The samples were exposed to a fixed relative (de-ionised) humidity of 90% at a temperature of 23 °C and a laminar air flow of 1.0 l/min. The high humidity level was chosen to simulate a corrosive environment, considering also that the chamber did not allow climate cycling, which is commonly used in corrosion tests to simulate outdoor conditions. The duration of the laboratory exposures was one, two or three months. The amines were sprayed on both sides of the samples at frequencies varying from weekly to daily. In the initial runs (sample no. 3 to 6, Table 2) this represented 10 to 17 years of maximum expected deposition to the ground outdoors, calculated by Eq. (1).

$$t_m = \frac{C \times V_a \times N_a \times t_e \times u}{D_{max} \times A} \tag{1}$$

Where  $t_m$  is the duration of maximum expected (modelled) MEA equivalent deposition to the ground (years), *C* is the concentration of the

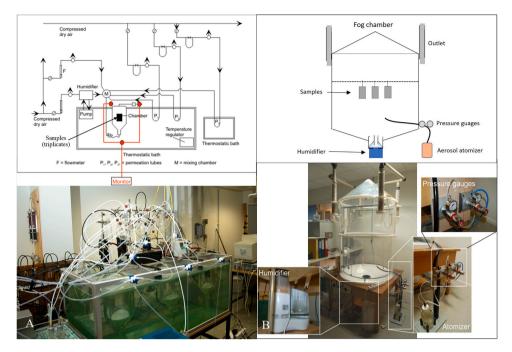


Fig. 1. The stable climate and pollution chamber (A) and fog chamber (B) used for controlled exposure to amines. With schematic diagrams shown above the photos.

experimentally applied (sprayed) amine solution (M),  $V_a$  is the volume of each application (l),  $N_a$  is the number of applications per month,  $t_e$  is the experimental exposure duration (months), u is the molar weight of the amine,  $D_{max}$  is the outdoor maximum modelled amine (MEA) deposition = 0.0016 g/m<sup>2</sup>× year, and A is the sprayed sample area = 0.03 m<sup>2</sup>.

The later runs were carried out with 100 times higher concentrations to observe any possible effects on the corrosion. These applied doses represented 6000 years (sample no. 13 and 21 Table 2), to 16,000-26,000 years (sample no. 9-11, 22, Table 2) of maximum expected MEA equivalent deposition to the ground. The higher ranges of the estimated values for the dose-years in the initial runs (14–17 years), and in the later runs (22,000-26,000 years), represented the assumed similar annual total mass deposition (1.6 mg/m<sup>2</sup> year) of exposures with the higher molecular weight DEA and AMP, than MEA. Considering the high doses and uncertainties in the experiments this is a technicality which seems of little significance for the interpretation of the results. To simulate a polluted environment, in seven of the experimental runs the samples were, in addition, exposed to a time averaged concentration of  $SO_2$  of 470 µg/m<sup>3</sup> emitted from a permeation tube into the inflowing air stream. SO<sub>2</sub> concentrations were much higher in Norway (and Europe) in the last part of the 1900th century than today, and do not represent the present most typical air pollution exposure (Kucera et al., 2007; EEA (European Environment Agency), 2018). It is, however, the generally most corrosive common single air pollutant (Kucera et al., 2007) and was therefore chosen. Annual average concentrations of SO2 are in most places in Europe today below 10  $\mu$ g/m<sup>3</sup>, and seldom above a few  $\mu$ g/m<sup>3</sup> in Norway, except very locally at industrial hot spots. Exceptions are, for example, the Silesia region between Poland and Czechia, and regionally in South Eastern Europe, where annual concentrations can still be higher (EEA (European Environment Agency), 2018). Two to three months of experimental exposure to an SO<sub>2</sub> concentration of 470  $\mu$ g/m<sup>3</sup> could therefore be assessed to represents 200-300 years of present "moderate industrial exposure". In the set up for continuous spraying in the fog chamber, the samples were humidified with a drinking quality tap water fog emitted from a humidifier giving 100% relative humidity and exposed to an amine aerosol spray with a number median diameter of about 0.3  $\mu$ m and mean particle size between 0.02 and 0.3  $\mu$ m (Karl and Lopez-Aparicio, 2010). The ions in the laboratory tap water were not determined. Table 1 compares the contents of the main ions in the tap water supply from the water work to the region of the experimental laboratory in 2020 (NRV/NRA, Rent drikkevann, Resultatene, 2020) with the measured annual average content in the rainwater in Oslo in 2018 (Grøntoft and Roux, 2020).

The much lower pH in rainwater than the tap water indicates, despite a seemingly generally lower ionic content, a higher corrosivity of the rainwater than the tap water. An approximate amount of 1 l per week of the amine solution was atomized into the fog in the chamber subjecting the wet metal samples to a fine aerosol spray and fog with the amines. A significant amount of the amine aerosol and fog deposited on the samples. This could be observed as the fine aerosol fog raised towards the samples during its spreading into and mixing with the water fog. The MEA aerosol mixing in the water fog was found to generate a bimodally distributed droplet population with a major mode at 8–10 µm diameter and a weaker mode between 20 and 30 µm (Karl and Lopez-Aparicio, 2010). The exact amount of emitted amine in the aerosol spray that deposited on the samples was however not known. A larger amount than was depositing on the samples, probably deposited on the chamber walls partly after having dissolved in the water fog. The amine concentration in the fog droplets depositing on the steel samples would depend on the mechanism of the droplet growth in the humid atmosphere and their coalescing to the size distribution at the time of impact, as influenced by the dissolved MEA. The concentration of the amines in the continuously impacting droplets would clearly be lower than in the initial MEA solution but was not determined. Even with a measure of the amine concentration in the fog droplets, a direct quantitative comparison of the amine exposure doses of the different wetting regimes in the two

### Table 1

The reported content of regional (laboratory) tap water and rainwater in Oslo, Norway.

Water source	Ionic content							
	pН	pH Conductivity		$Cl^ SO_4^{2-}$		Na		
		ms/m	mg/l					
Regional supply of laboratory tap water	7.7	8.9	8.4	3.5	0.33	3.0		
Rainwater in Oslo	5.5	2.4	2.8	1.3	0.55	1.5		

chambers would have been complicated. Therefore, the observed corrosion effects in the stable climate and pollution chamber and the fog chamber are not directly comparable by the, different, measures for the exposure doses, but should rather be compared by the change in the effects depending on the change in the doses (the derivatives).

### 2.2. Field test

Carbon steel samples were mounted on the 1st May 2011 for a one year outdoors exposure period on four Norwegian field stations; Skøyen-Oslo (urban background, UB), Borregaard (industrial, I), Birkenes (rural, R), and Tananger (coastal, C) (sample nos. 23–32 Table 1, and Fig. 2).

The samples were mounted at 45° and shielded from rain to avoid off washing of the applied amine solutions. At the Skøyen-Oslo (UB) station four sets of twelve samples were sprayed with MEA, DEA, AMP, and deionised water, respectively. Subsets of triplicate samples, of the twelve in each set, were exposed for three, six, nine and 12 months. On the three other stations MEA was sprayed or brushed (only Birkenes) to one, and de-ionised water to another, set of 4 samples. The amines and de-ionised water were applied every fourteen days to both sides of (over and under) the samples. The amine solutions had a concentration of  $6.5 \times 10^{-4}$  M. The exposures represented 65 to 110 MEA equivalent maximum deposition model years

Table 2 gives an overview of the experimental conditions in all the laboratory and outdoor exposures and includes the results from the weight measurements, for easy reference to the experiments. The weight loss, measured by chemical stripping, of the samples exposed in the laboratory was not significantly different from that of a "blank" unexposed steel sample and are therefore not given in Table 2. Except for one sample, no. 9, which was sprayed with the highest dose of MEA, and its control sample exposed to water.

### 2.3. Analysis of corrosion product layers

The samples were weighed before and after the exposures and the weight change was determined. When a metal corrodes it gains weight by the addition of oxygen and other trace elements in the corrosion product layer. The corrosion layer will wear in the ambient and the weight gain will be less than calculated from the pure metal loss and reaction to the corrosion products. If the wear is high the sample can lose weight. The corrosion amount is therefore commonly measured by the pure metal loss due to the corrosion and not by the less predictable corrosion layer formation. In the following a "weight gain" refers to an increased weight, and a "weight reduction" to a decreased weight, of the sample after exposure. A "weight loss" refers to the reduced weight of the metal measured after chemical stripping of the corrosion layer. The weight loss provides a direct measure for the corrosion effect of the environment. The weight change (gain or reduction) is interesting to measure as it allows additional interpretation of the corrosion layer formation and environmental wear on the corrosion.

All the samples were photographed after exposure with a small digital camera (Canon S90) in the same indoor shaded location with a mixture of light from fluorescent roof lamps at a distance of about two meters and outdoors daylight through a window at a distance of about one metre. The camera was set to automatic white balancing and the photos were not subjected to any further colour calibration or other adjustments. For every subset of samples exposed outdoors for 12 months, and applied type of amine solution at the Skøven-Oslo (UB) station, and set of samples on the other stations, one sample was assigned for later physical observation and analysis. Some of the corrosion was scraped off a number of the remaining samples and analysed with Scanning Electron Microscopy and X-ray analysis (SEM-EDX), to provide high magnification images, electron count spectrums showing the peaks for the elements at different electron energies, and tables giving the respective weight% and atom% of the elements in the corrosion product layers. The energy of the electron beam was set to obtain as much as possible of the x-ray scattering used for the elemental analysis from the sampled corrosion layer rather than from the carbon tape used for the mounting. Examination of the mineralogical composition of the corrosion was not performed.

The corrosion products were then chemically stripped off the samples, that had been exposed in the laboratory and outdoors, by immersing the samples in Clark's solution (100 ml hydrochloric acid, HCl, 2 g antimony trioxide,  $Sb_2O_3$  and 5 g tin chloride,  $SnCl_2$ ) for the required duration (Wade and Lizama, 2015). The samples were then weighed again to determine the weight loss due to the corrosion. The effect of the amines was analysed by comparing the weight change after exposure and weight loss after stripping, and the elemental content of the corrosion layers, of samples sprayed with aqueous amine solution or water.

### 2.4. Air pollution and climate

From larger exposure programs and dose-response studies it is known that the major environmental parameters that influence the corrosion of steel are the precipitation amount and its acidity, the temperature, the SO<sub>2</sub> concentration in air (Kucera et al., 2007; ISO 9225:2012, 2020) and the dry deposition of chloride (e.g. Kubzova et al., 2021). Therefore, these parameters were measured on the field stations in parallel with the corrosion exposures. The general particle concentration (PM<sub>10</sub>) has also been found to influence the corrosion of steel in multi-pollutant environments with less SO<sub>2</sub> (Kucera et al., 2007). The PM effect would to some extent, and especially in coastal and chloride exposed industrial and traffic environments, be represented by chloride. The generic PM effect has been found to be relatively low compared to that of the other pollutants (ISO 9225:2012, 2005), and PM is commonly measured with relatively expensive instrumental methods. In this work the aerosol deposition was measured with passive means, which do not provide values for the concentration in air but have the advantage of directly measuring the load that materials are exposed to and give



Fig. 2. The outdoor exposure stations (A) and their locations (B). The samples were mounted under precipitation shields. The application of the amines (MEA, DEA or AMP) and pure water to the samples is noted.

### Table 2

Samples, experimental conditions, and corrosion weights. All the solutions were made with de-ionised water (noted as  $H_2O$ ).

Sample# (no. of replicates S=Swedish, N=Norwegian DC01 steel)	Exposure		Results					
	Application compound	Concentration: Amine (M), $SO_2(\mu g/m^3)$	Duration (months)	Appl. frequency (#/week, C=continuous spray)	Amine dose (g, C: M × month)	Maximum deposition model years	Weight change (g)	Weight loss after stripping (g)
Laboratory test								
Steel								
Dry exposure								
1 (3,S)	No, Dry	0	1	1	0	-	$0.008\pm0.002$	
2 (3,N)	SO <sub>2</sub> Dry	470	2	_	0	-	$0.4\pm0.2$	
Discontinuous amine spra	ying - Lower amine	e dose						
3 (3,S)	DEA	0.00065	1	1	0.0005	10	$0.0007 {\pm} 0.0025$	
4 (3,S)	AMP	0.00065	1	1	0.0008	17	$0.02{\pm}0.03$	
5 (3,S)	MEA	0.00065	1	1	0.0007	14	$0.0003{\pm}0.0006$	
6 (3,S)	$MEA + NH_3$	0.00065 (both)	1	1	0.0005	10	0	
Discontinuous amine spra	ying - Higher amin	e dose						
7 (3,N)	$H_2O$		1.5	5	0	-	$0.057{\pm}0.018$	
8 (3,S)	$H_2O$		3.3	5	0	-	$0.028{\pm}0.002$	$0.20 {\pm} 0.005$
9 (3,S)	MEA	0.065	3.3	5	0.8	16,000	$0.012{\pm}0.002$	$0.030{\pm}0.004$
10 (3,N)	AMP	0.065	3	5	1.0	22,000	$-0.0003 \pm 0.0043$	
11 (3,N)	DEA	0.065	3	5	1.2	26,000	$-0.010{\pm}0.004$	
12 (3,N)	$SO_2 + H_2O$	470	2	3	0	-	$0.8\pm0.4$	
13 (3,N)	$SO_2 + MEA$	470 + 0.00065	2	3	0.3	6000	$0.6\pm0.3$	
Continuous amine sprayin	g							
14 (4,S)	H <sub>2</sub> O		1	С	0	_	$0.043 {\pm} 0.009$	
15 (3,S)	MEA	0.00065	1	С	0.00065	_	$0.004{\pm}0.0015$	
16 (3,S)	DEA	0.00065	1	С	0.00065	_	$0.005 {\pm} 0.003$	
17 (4,N)	AMP	0.065	1	С	0.065	_	$0.012{\pm}0.008$	
18 (1.S)	AMP	0.065	1	С	0.065	_	0	
Copper								
19(1)	SO <sub>2</sub> Dry	470	2		0	-	-0.0047	
20 (1)	$SO_2 + H_2O$	470	2	3	0	-	0.047	
21 (1)	$SO_2 + MEA$	470 + 0.00065	2	3	0.3	6000	0.017	
22 (1)	$SO_2 + DEA$	470 + 0.065	3	5	1.2	26,000	-0.11	
Field test. Sk=Skøyen-Os		regard (I), Bi=Birkene	s (R), Ta=Tanan	ger (C)				
23 Sk (3,S)	H <sub>2</sub> O	0	12	0.5	0		0.56	$0.77 {\pm} 0.03$
24 Sk (3,S)	MEA	0.00065	12	0.5	0.003	65	$0.56{\pm}0.02$	$0.75 {\pm} 0.04$
25 Sk (3,S)	DEA	0.00065	12	0.5	0.0054	110	$0.57{\pm}0.02$	0.79
26 Sk (3,S)	AMP	0.00065	12	0.5	0.0046	100	$0.58{\pm}0.03$	$0.78{\pm}0.02$
27 Bo (4,S)	$H_2O$	0	12	0.5	0		$-1.2\pm0.9$	$13.3\pm0.5$
28 Bo (4,S)	MEA	0.00065	12	0.5	0.003	65	$-1.9\pm0.3$	$14.0\pm0.2$
29 Bi (4,S)	$H_2O$	0	12	0.5	0		$0.85{\pm}0.01$	$1.56{\pm}0.03$
30 Bi (4,S)	MEA	0.00065	12	0.5	0.003	65	$0.82{\pm}0.02$	$1.57{\pm}0.05$
31 Ta (4,S)	$H_2O$	0	12	0.5	0		$8\pm 2$	$18{\pm}2$
32 Ta (4,S)	MEA	0.00065	12	0.5	0.003	65	$7\pm1$	$20{\pm}1$

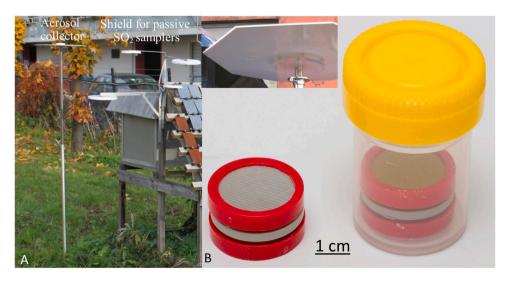


Fig. 3. The aerosol collector and shields (A) for the passive diffusive gas sampler (B). The top insertion shows the underside of the shield of the aerosol collector with the holder for the aerosol filter.

respective values for the separate (water soluble) ions.

The  $SO_2$  in air, and the anions and cations in deposited aerosol were passively sampled under precipitation shields during the 12 months through the exposure year at the four exposure stations (Fig. 3A). The  $SO_2$  sampling was performed with duplicate diffusive samplers of the IVL batch type produced at NILU (Fig. 3B) containing alkali impregnated gas absorption filters (Ferm, 1991).

The SO<sub>2</sub> concentration was calculated from the amount of sulphate collected on the filters as determined by ion chromatography, the geometry of the sampler and the diffusion coefficient of SO<sub>2</sub>. The aerosol sampling was performed with an aerosol collector (Anda and Haagenrud, 1984) on a glycerol impregnated Teflon filter with a diameter of 10 cm fixed horizontally on a plate one cm below the precipitation shield. The ionic composition (Cl<sup>-</sup>, NO<sub>3</sub>-N, SO<sub>4</sub><sup>2-</sup>-S, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>-N, K<sup>+</sup>,  $Mg^{2+}$  and  $Ca^{2+}$ ) was determined by subsequent washing of the filter in de-ionised water and analysis by ion chromatography. The pH was measured in the washing water with a glass electrode. One prepared aerosol filter was stored in the laboratory in its plastic zipper bag during one month as a blank and analysed with the same procedure as the exposed samples, returning a near zero (insignificant) value for the ions. Annual average values for the precipitation and temperature were collected from the Norwegian Meteorological Institute stations closest to the field test stations (Table 4) (eKlima 2020). The effect of the environment on the corrosion was analysed by single correlation of the pollution and climate parameters on the measured first-year corrosion on the stations.

### 3. Results

Due to the many diverse results presented below it was decided to provide a short overviewing introduction. First, the effect of amine spraying in reducing the weight gain (or weight at high doses) of laboratory exposed samples, in unpolluted (Fig. 4) and SO<sub>2</sub> containing (Fig. 6) atmospheres, is shown. An increase in the effects rate with time is indicated in Fig. 5. Images of the exposed samples are shown in Fig. 7. A comparison of the weight change and weight loss after chemical stripping of samples exposed outdoors (imaged in Fig. 10) is shown in Figs. 8 and 9, indicating reduced weight change (or weight), increased weight loss after stripping, and some increase in the winter corrosion, of samples exposed to amines as compared to controls. The elemental composition of the corrosion product layers is then shown in Fig. 11, by the SEM-EDX results for a sample exposed in the industrial location (Borregaard), where the corrosion amount and detected sulphur in the corrosion (different from other locations) could be explained by the higher SO<sub>2</sub> ambient concentration. Finally, the results from the environmental measurements are reported, in Fig. 12 and Table 4, as a basis for the following discussion.

### 3.1. Laboratory tests

Fig. 4 shows the weight change of the steel samples exposed in the

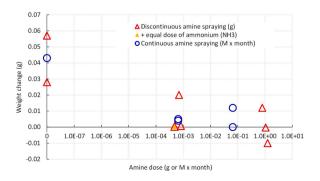


Fig. 4. Weight change of steel samples exposed to amines.

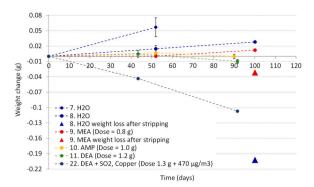


Fig. 5. Time development of the weight change of steel samples exposed to amines, and one copper sample exposed to amine and  $SO_2$  (for sample nos. see Table 2).

laboratory to different applied doses of the amines.

As no significant difference was observed in the weight change of samples sprayed with the different amines (MEA, DEA and AMP, Table 2) it is not distinguished between them in the figure. It can be observed that the weight change decreased with increasing amine doses and that the weight of a few samples exposed to the higher doses was slightly reduced. At a dose representing ~10–15 years of maximum expected MEA exposure to the ground (~1 × 10<sup>-3</sup> g, Table 2) due to emission from a carbon capture plant, the weight gain decreased with 50% to 100%. The considerably higher reported pH of local tap water, as used in the continuous humidification in the laboratory (pH = 7.7, Table 1) than of rain water (pH ~ 5.5, Table 1), may have led to some overestimation of the continuous amine dose effect observed in Fig. 4 (as compared to the effect with precipitation water and assuming that the weight reducing effect is associated with the amine alkalinity).

Fig. 5 shows the time development of the weight change of steel samples exposed to water and amines (for which several measurement were made over time, and for which the end points were also shown in Fig. 4), the weight loss after stripping of steel sample no. 9 and its control exposed to water (no. 8), and the weight change of one copper sample exposed to SO<sub>2</sub> and amine. The largest weight gain observed on any steel sample, after about 50 days spraying with water (no. 7), is also shown.

It is seen in the figure that the samples exposed to water only (blue) gained weight more quickly and lost more weight by the stripping than the samples exposed to the amine solutions, indicating more corrosion of the samples exposed to the water only. It is also seen that the weight change was ultimately less for the samples (of 9, 10 and 11) that were exposed to the higher doses of the amines (two of the samples lost weight), and the rate of the weight change (reduction) of the copper sample is clearly seen. Finally, it is seen that the weight loss after stripping of the corrosion of the one steel sample exposed to the highest applied MEA dose (no. 9) was significantly larger than that of a sample exposed to de-ionised water (no. 8) (as measured by non-overlapping ranges for the standard deviations of triplicate measurements, Table 2).

Fig. 6 shows the weight change of steel and copper samples exposed in the laboratory to  $SO_2$  (470 µg/m<sup>3</sup>) and different applied doses of the amines.

The pH measured in the de-ionised water and amine solutions before spraying is noted. In addition, the pH was measured to 9.3 in the DEA solution having dripped off a copper sample (no. 22) during the exposures (see Fig. 7). The addition of SO<sub>2</sub> to the exposures together with the water spraying, increased the weight of both steel and copper samples. The spraying with an amine solution instead of the pure water, in the SO<sub>2</sub> containing atmosphere, reduced the weight change in comparison with the water spraying. At the highest amine (DEA) exposure doses, representing 16,000 years maximum expected MEA exposure to the ground ( $\sim$ 1.2 g, Table 2), both a steel (Fig. 4) and a copper sample lost weight, with the weight reduction being much larger for the copper (but

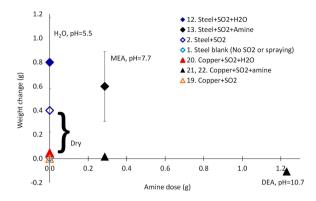


Fig. 6. Corrosion amounts on steel and copper samples exposed to amines in an  $SO_2$  containing atmosphere (sample nos., see Table 1).

in this case in an  $SO_2$  containing atmosphere, Fig. 6) and showing dissolution of the copper without the building up of a corrosion layer that could compensate for the weight reduction.

Fig. 7 shows photos of the steel and copper sample surfaces after the exposures, and a photo of the dark blue coloured off-dripping solution from the copper sample (no. 22) to the bottom plate in the chamber, that occurred after the spraying with the transparent colourless DEA solution

in the SO<sub>2</sub> containing atmosphere.

The contents of this off-dripping were not determined, but the bluish colour indicates copper dissolved from the sample. The yellowish driedup spots were from earlier off-dripping from steel samples. The figure shows, generally, a reduced amount of corrosion on the samples exposed to the amines, to be discussed below, and indication of colour differences between samples exposed to SO<sub>2</sub>, water and different amines.

### 3.2. Field test

Fig. 8 shows the first-year weight change and weight loss after stripping of the sheltered samples sprayed with de-ionised water and with MEA on the four stations.

A classification of the corrosion rates of the samples sprayed with MEA, according to ISO 9223, is given in Table 3. This does not exactly represent the open unmanipulated environmental corrosion according to ISO 9223, but the classes are the same as has been found for such standard exposures on the stations.

As some of the corrosion products were lost during the exposure, the weight change (A) was significantly lower than the weight loss measured after the stripping (B). A comparison of the values of the samples sprayed with de-ionised water and with MEA, indicated a systematic difference between them, although with a low significance. On the two stations with high corrosion (Borregaard (I) and Tananger (C)),

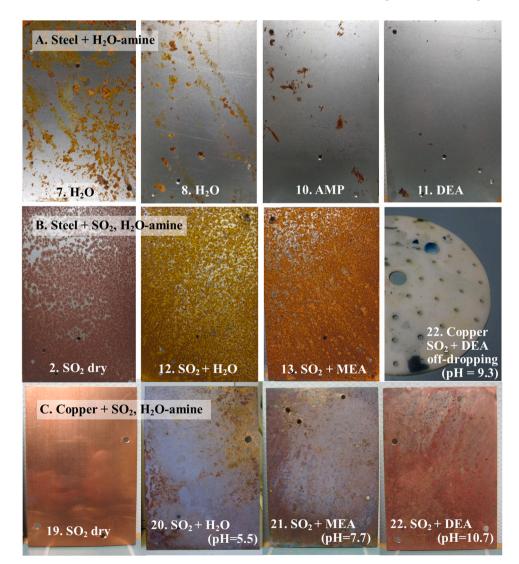
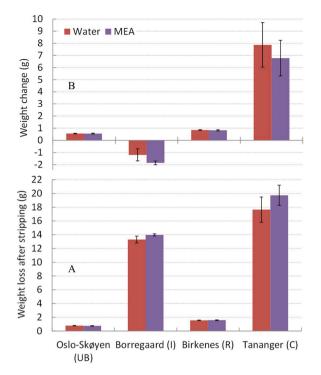


Fig. 7. Photos of steel and copper samples after exposures in the laboratory (Table 2).



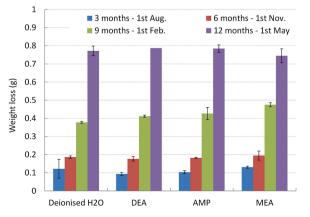
**Fig. 8.** First-year corrosion amounts of steel samples sprayed with water and MEA solutions in sheltered position on four Norwegian stations with different atmospheres. Measured as weight change after exposure (A), and weight loss after stripping (B).

### Table 3

The ISO 9223 corrosion class determined from the measured first-year corrosion of carbon steel at the stations.

	First-year weight loss (g/m <sup>2</sup> year)	Class (1–5)	Description
Skøyen-Oslo (UB)	24.8	2	Low
Borregaard (I)	465.8	4	High
Birkenes (R)	52.4	2	Low
Tananger (C)	658.0	5	Very high

and also on the Birkenes (R) station, the weight loss after stripping of the samples sprayed with MEA was higher than of those sprayed with water, with a larger difference on the Tananger (C) station with the highest corrosion (Fig. 8A). For the weight change the opposite situation was observed, with a reduced weight gain or total weight (Borregaard) of the samples sprayed with MEA as compared to those sprayed with water



**Fig. 9.** Weight loss after stripping of steel samples exposed for 3, 6, 9 and 12 months, with demounting dates, at the Skøyen-Oslo (UB) station.

### (Fig. 8B).

Fig. 9 shows the time dependence of the weight loss after stripping of the triplicates sprayed with the amines (DEA, AMP and MEA) and with de-ionised water on the one station with three monthly samples, Skøyen-Oslo (UB), where the lowest corrosion was measured.

The figure shows the lowest corrosion from three to six months in the summer and the highest corrosion in the later winter and spring periods. Only the samples which were demounted after nine months of exposure, in the wintertime on the 1st of February, showed ranges for the standard deviation of the samples sprayed with the amines which did not overlap with those of the samples sprayed with the de-ionised water. As was found in the laboratory experiments, the results from the outdoor stations indicated that the spraying with MEA had some corroding effect on the samples, and in dissolving, and increasing the off running of the corrosion.

Fig. 10 shows photos of the samples sprayed with MEA after one year of outdoor exposure on the stations.

A difference from the samples sprayed with water was not observable by the eye. The corrosion products had a different appearance on the four stations. The samples from Tananger (C) and then Borregard (I) had the coarsest corrosion layers. The upper sides were smoother than the undersides. The undersides of the samples from Tananger (C) had coarse and thick dark/blackish layers that mostly attached to the samples. The upper sides, and even more of the undersides, of the samples from Borregard (I) had large dark/blackish areas where the corrosion seemed to have loosened. On the Skøyen-Oslo (UB) station the corrosion on the upper side had a dark reddish "spotted" appearance whereas little corrosion was observed on the underside. The samples from Birkenes (R) had the evenest corrosion of the all the sites, with a light reddish corrosion layer on the upper side and a slightly darker corrosion in small evenly distributed spots on the underside.

The upper- and under-sides of samples no 23 to 30, which had been sprayed with MEA or water for one year on the Borregard(I), Skøyen-Oslo (UB), and Birkenes (R) stations (Table 2, Fig. 10), were imaged and analysed with SEM-EDX. The samples from the Tananger (C) station were not observed with SEM-EDX due to the special situation with direct splashing from the sea and a limitation in the available resources for this analysis. Fig. 11 shows the electron count spectrum, weight% and atom % of the elements in the corrosion of a sample exposed on the Borregard (I) station.

The carbon is mainly from the sample fixing tape. In all the samples at all the stations iron and oxygen, besides the carbon was detected as the major elements. The relative atomic content (%) of iron and oxygen (Fe/O) was for all the samples approximately  $\frac{1}{2}$ , which corresponds to iron(II) hydroxide, Fe(OH)<sub>2</sub>, or some form of iron(III) oxide-hydroxide, x-FeOOH. In one sample at Skøyen-Oslo (UB) one atom% of silicon was detected. At the Borregard (I) station the inclusion of 1.8 to 4.5 atom% of sulphur was measured in all the samples, except the upper side of one sample sprayed with water where 0.5–0.8% atom% of sulphur was measured and in addition ~0.25 atom% chloride was detected. The reported error in the sulphur results were in the range ~10–30%. For the more abundant elements it was lower. For the barely detectable elements (Si and Cl) it was approaching the reported result values. No nitrogen, which could indicate that the amines participated in the corrosion reactions, was detected in any sample.

### 3.3. Environment

Meteorology relevant geo-location data, the annual averages of the temperature,  $SO_2$  concentration, and pH in deposited aerosol, and the annual amount of precipitation and ions in deposited aerosol, measured close to or on the field exposure stations, are given in Table 4 and Fig. 12 (the ions).

The missing cations are reported as carbon in bicarbonate ( $HCO_3^--C$ ), calculated from the charge balance. The  $HCO_3^-$  deposition therefore appears as negative when a higher total anion than cation charge was

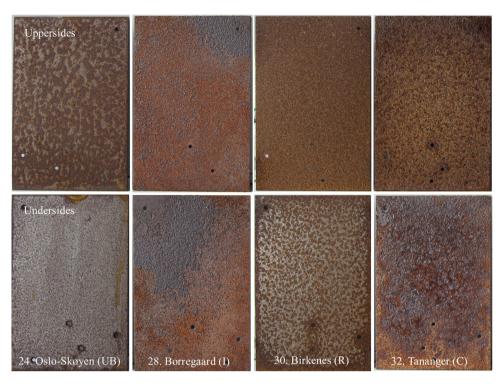


Fig. 10. Photos of samples after outdoor exposures.

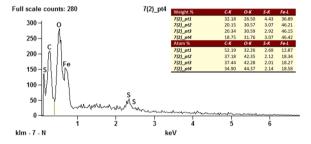


Fig. 11. The electron count spectrum and elemental weight% and atomic% in the corrosion of a sample from the Borregaard (I) station (7(2)\_pt4 = image analysis area no. 4, of the 2nd image of the 7th SEM sample).

reported from the analysis. The monthly values for the SO<sub>2</sub>, pH and ions are given in Table A1 in the Appendix.

The annual average temperature at the meteorological stations close to the exposure sites varied from 5 °C at Senumstad (Birkenes) to 9 °C at Sola (Tananger). The annual average precipitation varied from 988 mm at Oslo-Blindern (Skøyen-Oslo) to 1743 mm at Senumstad (Birkenes). The annual measured amounts of ions in deposited aerosol were two orders of magnitude (~ one hundred times) higher at Tananger (C) than at the other three stations. During seven months in the colder seasons at least one of the duplicate SO<sub>2</sub> passive samplers on the Tananger (C) station was observed to contain high salt amounts, which resulted in very high estimated SO<sub>2</sub> concentrations (100 to 1400  $\mu$ g/m<sup>3</sup> in single samplers, Table A1) that could not represent the SO<sub>2</sub> air concentration. The SO<sub>2</sub> values for Tananger (C) were therefore not reported in Table 4. This could be explained by wetting of the samples by sea spray, which was reflected in the high measured chloride and total aerosol deposition in the autumn and winter (Table A1). The sea spray is typical for high wind episodes during these seasons on the west coast of Norway (Grøntoft and Svenningsen, 2009). The amounts of deposited ammonium on the Tananger (C) station were much higher than on the other three stations (Table 4, Fig. 12), with the highest values in May, June, September, and October. The reported monthly average concentrations

### Table 4

Geo-location, meteorological and air quality data at the stations.

Environmental	Meteorological station - field exposure station									
parameter	Oslo, Blindern – Skøyen (UB)	Sarpsborg – Borregard (I)	Senumstad – Birkenes (R)	Sola – Tananger (C)						
Distance from field- to met station (km)	3.5	7	5	9						
Altitude (m)	10	40	190	1.5						
Temperature (°C)	7.7	8.1	5	9.1						
Precipitation (mm)	988	1122	1743	1552						
	Skøyen- Oslo	Borregaard	Birkenes	Tananger						
SO <sub>2</sub> (μg/m <sup>3</sup> )	$\textbf{3.0} \pm \textbf{0.2}$	$63\pm8$	$\textbf{4.0} \pm \textbf{0.3}$	n.a.						
pН	5.3	4.8	5.3	5.9						
Ions in aerosols, tota	Ions in aerosols, total annual deposition $(mg/m^2 d, Mol atomic charge x 1000 /m^2 d)$									
Cl <sup>-</sup>	7.4, 0.21	25, 0.70	5.0, 0.14	2300, 66						
HCO <sub>3</sub> -C	8.9, 0.15	-1.9, -0.03	3.0, 0.05	1800, 30						
NO <sub>3</sub> -N	1.1, 0.08	1.3, 0.09	0.4, 0.03	6.1, 0.44						
$SO_4^{2-}-S$	1.1, 0.07	12, 0.76	0.3, 0.02	120, 7.6						
Na <sup>+</sup>	3.9, 0.17	8.4, 0.37	3.1, 0.14	1500, 63						
NH <sub>4</sub> -N	0.7, 0.05	12, 0.85	0.04, 0.003	230, 17						
K <sup>+</sup>	1.3, 0.03	0.8, 0.02	1.0, 0.03	92, 2.3						
Mg <sup>2+</sup>	0.4, 0.03	0.9, 0.07	0.4, 0.03	180, 15						
Ca <sup>2+</sup>	0.4, 0.22	4.3, 0.22	0.9, 0.04	110, 5.7						

of SO<sub>2</sub> did not correlate with the deposition of the nitrogen containing ions NH<sup>4</sup><sub>4</sub>-N and NO<sup>-</sup><sub>3</sub>-N (nitrogen in ammonia and nitrate), as with the values for the other ions. It seems a nearby source, different from the sea spray, gave increased deposition of ammonium in the spring/summer and autumn. The source was not identified. It may have been emissions from agriculture. An elevated pH (= 7–9) was measured from November to January, which correlated strongly with the deposition of ions from sea spray, but not with the nitrogen containing ions.

The SO<sub>2</sub> concentration and amounts of deposited sulphate SO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup> and NH<sub>4</sub><sup>-</sup> ions were considerably higher at Borregaard (I) than at

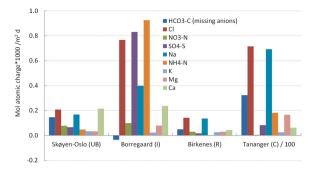


Fig. 12. The annual deposition of ions in aerosol on the stations.

Skøyen-Oslo (UB) and Birkenes (R), and from September to November when the  $SO_4^{2-}$  and total ion-deposition was the highest, the pH was the lowest (Table A1). This was probably due to emissions from the nearby cellulose plants. The amounts of deposited ions in aerosol were slightly higher at Skøyen-Oslo (UB) than at Birkenes (R), but the annual average  $SO_2$  concentration was measured to be slightly higher at Birkenes (R), which is more exposed to long-range transported air pollution from the European continent. The annual average pH was measured to be the same on both these stations.

### 4. Discussion

In the laboratory, the corrosion of both steel and copper samples was observed to increase, as measured both by the weight increase and weight loss after stripping, when the samples were exposed to water spray and then when SO<sub>2</sub> was added to the atmospheres. The addition of amines to the spraying water seemed to have both a corrosion inhibiting and dissolving effect. Amino groups can displace water molecules on metal surfaces and form hydrophobic films that protect against corrosion (Chen and Yang, 2019; Dariva and Galio, 2014). At the lower doses and pH of the amines (pH = 7.7 and representing 10 years of maximum modelled MEA deposition) they probably formed a thin corrosion inhibiting film on the surface that hindered the oxidation of the metal. They seem also to have had a dissolving effect on the corrosion layer and possibly on the metal substrate. The dissolving effect was observed to increase with increasing amine dose and pH until at the highest applied dose (pH= 10.7, and representing 16,000 years of maximum modelled MEA deposition) a net dissolving effect was observed on both the corrosion layer and metal substrate, which reduced the total weight of both steel, and of copper samples exposed in an SO<sub>2</sub> containing atmosphere. When SO<sub>2</sub> was added to the controlled atmospheres the corrosion increased and the inhibition and/or corrosion dissolving effect of the amines seemed to increase, as measured by the weight changes (Figs. 4 and 6). For the steel, the experiments included too few samples exposed in the SO<sub>2</sub> containing atmosphere and too small effects to conclude about this. For the copper, a very significant effect of the amines was observed. The weight gain of the samples was reduced with increasing amine dose and pH, until at the high application dose of amine (DEA) and pH (= 10.7) the corrosion layer and copper substrate were dissolved. In humid SO<sub>2</sub> containing atmospheres copper sulphate and different hydrated copper sulphate hydroxides are known to be formed on copper (Graedel and Leygraf, 2000; Ericsson and Sydberger, 1977). Copper typically reacts with ammonia to form an intensely blue copper/ammonium complex (Davies, 2006). With the application of the amines, a copper amine or ammonium complex, possibly also including sulphate ions, seems to have been formed. At low doses, the amines may have inhibited the corrosion, but at higher doses DEA clearly increased the dissolution of the corrosion products and the copper substrate, and the off running of a copper containing solution. The slightly reduced pH (= 9.3) of the bluish solution having dripped off the copper samples after spraying with DEA in the SO<sub>2</sub> containing atmosphere, indicated

neutralization by the acidic  $SO_2$  and possibly also due to the reaction with the copper.

Outdoors, the major difference in the values of the first-year corrosion of the steel samples was between the much higher corrosion on those exposed on the Tananger (C) and Borregaard (I) stations, than on the Skøyen-Oslo (UB) and Birkenes (B) stations, irrespective of the spraying with MEA or water. A corroding, and corrosion and/or the metal substrate dissolving and off-running, effect of the amines was indicated (at low significance) by the lower weight change and higher weight loss after stripping of the samples sprayed with MEA than with water in aggressive environments on the Tananger (C), Borregaard (I) stations (ISO classes 5 and 4) and on the Birkenes (R) station (ISO class 2) (Table 2, Fig. 8), and which were demounted in the winter (after 9 months) on the Skøyen-Oslo (UB) station (ISO class 2) (Fig. 9). Accumulation of the amine on the steel surfaces after spraying may have contributed to some freezing point depression and increased the time of wetting and corrosion of the samples in the cold season with frost. The relative importance of the dissolving and liquidizing effects of the amines would depend on meteorology, natural aerosol deposition and air pollution. The liquidizing effect seems more uncertain in the situations with sea spray on the Tananger (C) station and relatively high aerosol deposition on the Borregaard (I) station. As no nitrogen was observed in the corrosion of the samples from Skøyen-Oslo (UB), Borregaard (C) and Birkenes (R), which were analysed with SEM-EDX, the amines and possible nitrogen containing reaction products seem to have remained in solution or been dissolved, to off-run from the samples. This was also indicated by the effect of the amine spraying in the laboratory and outdoors in reducing the weights of the samples.

The highest corrosion, measured at Tananger (C), seems to be explained by the much higher exposure load of chlorides and other ions in aerosol from sea spray. The higher temperature, and high precipitation, at Tananger (C) have contributed to the high corrosion. The different graininess of the corrosion on the stations may be, mainly, related to the wetting of the samples as affected by the deposition of aerosol particles and air pollution. The sea spray and sea salt deposition on the Tananger (C) station was probably the main reason for the coarser structure of the corrosion on this station. The somewhat finer grained, uniform, and yellowish-reddish corrosion at Tananger (C), and more clearly at Birkenes (R) (see below), than on the Skøyen-Oslo (UB) station may have been due to less anthropogenic air pollution (Tidblad et al., 2014) including dust, than at Skøyen-Oslo (UB).

Fig. 13 shows the correlations between single environmental parameters and the measured weight loss of the samples after stripping, on the three other stations than Tananger (I).

The higher weight loss on the Borregaard (I) station correlated with the higher SO<sub>2</sub> concentration and deposition of chloride in aerosol, and the lower pH, at this station. Chloride and SO<sub>2</sub> are well known to increase corrosion of carbon steel (e.g. Graedel and Leygraf, 2000; ISO 9225:2012, 2020). The high SO<sub>2</sub> concentration on the Borregaard (I) station was probably the main reason for the different appearance of the corrosion (Fig. 10). The presence of atmospheric SO<sub>2</sub> increases the rate of formation of ferrous oxides (x-FeOOH) (Wang et al., 1997) and leads to the presence of sulphate ions and ultimately to the formation of iron sulphate (FeSO<sub>4</sub>), which is mainly found in layers at the metal surface (Graedel and Leygraf, 2000; Syed, 2006). The inner blackish more solid layer probably contained much of the sulphur, as more or less hydrated iron sulphate, Fe(SO<sub>4</sub>)·nH<sub>2</sub>O, with the looser off-scaling upper layer being the typical reddish iron oxides.

The slightly higher corrosion measured at the Birkenes (R) than Skøyen-Oslo (UB) station, where the load of ions in aerosol was slightly higher (Table 4), was probably due to a somewhat higher SO<sub>2</sub> concentration and more precipitation on the Birkenes (R) station (Table 4). The samples exposed at Birkenes had the finest grained, uniform, and reddish corrosion. This station is located at an elevation of 450 m, with the highest amount of rain, and coldest and expected most foggy conditions (Table 4), probably leading to more situations with uniform wetting by

### Table A1

Monthly values of  $SO_2$ , pH and dry deposition of ions. The missing cations are reported as bicarbonate ( $HCO_3^--C$ ), from the charge balance, and appears as negative in the cases when a higher total anion than cation charge was reported in the analysis. At Borregaard (I) in October and November the sampling period was two months, and the same value for the ion deposition is therefore reported for both these months. The  $SO_2$  value represents the average of duplicates. The ions were collected on one filter in each month on each station. The values for bicarbonate ( $HCO_3^-$ ), nitrate ( $NO_3^-$ -) and sulfate ( $SO_4^{2-}$ ) are reported as their carbon (C), nitrogen (N) and sulphur (S) content.

Skøyen-Oslo (UB)	$SO_2$	SO <sub>2</sub> stdv	pН	HCO <sub>3</sub> <sup>-</sup> C	$Cl^{-}$	NO <sub>3</sub> <sup>-</sup> N	$SO_4^{2-}-S$	Na <sup>+</sup>	NH4-N	$\mathbf{K}^+$	$Mg^{2+}$	$Ca^{2+}$
Month	$\mu g/m^3$		-	mg/m <sup>2</sup> d								
5	3.0	0.03	5.2	0.12	0.48	0.09	0.13	0.23	0.001	0.36	0.06	0.29
6	2.8	0.1	5.2	0.05	0.20	0.07	0.04	0.13	0.002	0.11	0.03	0.14
7	3.1	0.1	5.1	0.01	0.23	0.08	0.03	0.12	0.002	0.12	0.02	0.10
8	3.0	0.4	5.4	1.5	0.33	0.002	0.002	0.21	0.002	0.16	0.04	2.34
9	2.4	0.3	5.2	0.02	0.16	0.05	0.03	0.11	0.002	0.04	0.02	0.09
10	2.9	0.1	5.3	0.02	0.59	0.16	0.09	0.31	0.002	0.14	0.04	0.29
11	2.3	0.2	5.1	-0.22	1.6	0.39	0.40	0.44	0.34	0.15	0.08	0.54
12	n.a.	n.a.	4.9	0.09	0.28	0.02	0.04	0.21	0.002	0.03	0.04	0.13
1	2.9	0.00	5.1	0.06	0.67	0.04	0.06	0.39	0.13	0.02	0.01	0.05
2	2.7	0.2	5.4	0.08	1.4	0.07	0.13	0.85	0.16	0.09	0.03	0.11
3	3.0	0.1	6.0	0.04	0.92	0.05	0.04	0.56	0.03	0.03	0.02	0.13
4	4.5	0.6	5.5	0.004	0.51	0.07	0.05	0.31	0.002	0.08	0.02	0.11
Average	3.0	0.2	5.3	1.8	0.61	0.09 NO <sup>-</sup> N	$0.09 \\ SO_4^{2-}-S$	0.32	0.06	0.11 v+	0.03 Mg <sup>2+</sup>	0.36 Ca <sup>2+</sup>
Borregard (I)	SO <sub>2</sub> 107	SO <sub>2</sub> stdv 19	рН 4.9	HCO <sub>3</sub> -C -0.39	Cl <sup>-</sup> 3.1	NO <sub>3</sub> -N 0.12	$50_4$ -5 0.75	Na <sup>+</sup> 0.49	NH <sub>4</sub> +N 0.84	K <sup>+</sup>	Mg 0.07	
5 6	71	4.7	4.9 5.0	-0.39 0.08	3.1 1.4	0.12	0.75	0.49	0.84	0.10 0.05	0.07	0.43 0.42
7	71	6.9	4.9	-0.11	0.5	0.09	0.33	0.41	0.30	0.03	0.03	0.42
8	87	14	5.0	0.02	0.9	0.06	0.35	0.20	0.38	0.04	0.03	0.21
9	67	2.2	4.6	-0.12	3.9	0.15	1.8	1.2	1.8	0.15	0.14	0.39
10	56	0.4	4.4	-0.07	4.4	0.18	2.2	1.9	2.0	0.11	0.19	0.61
11	66	5.2	4.4	-0.07	4.4	0.18	2.2	1.9	2.0	0.11	0.19	0.61
12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1	89	15	4.6	-0.02	1.1	0.09	0.87	0.44	0.78	0.04	0.03	0.22
2	9.6	11	5.3	0.22	1.7	0.11	1.29	0.57	1.5	0.08	0.05	0.38
3	46	0.6	5.0	0.04	1.7	0.11	0.90	0.46	0.99	0.04	0.05	0.40
4	27	9.1	5.0	0.04	1.7	0.11	0.90	0.46	0.99	0.04	0.05	0.40
Average	63	8.0	4.8	-0.38	2.3	0.12	1.1	0.76	1.1	0.08	0.08	0.39
Birkenes (R)	$SO_2$	SO <sub>2</sub> stdv	pН	HCO <sub>3</sub> <sup>-</sup> C	$Cl^{-}$	NO <sub>3</sub> -N	$SO_4^{2-}-S$	$Na^+$	NH <sub>4</sub> -N	$K^+$	$Mg^{2+}$	Ca <sup>2+</sup>
5	17	0.7	5.2	0.06	0.39	0.03	0.02	0.22	0.002	0.11	0.03	0.09
6	3.1	0.1	5.0	0.03	0.16	0.002	0.002	0.07	0.002	0.06	0.01	0.04
7	2.5	0.2	5.1	0.04	0.23	0.00	0.002	0.12	0.002	0.04	0.02	0.05
8 9	2.9 2.2	0.3 0.3	5.0 5.2	0.09 0.08	0.39 0.46	0.02 0.002	0.03 0.02	0.31 0.30	0.002 0.002	0.03	0.04 0.04	0.08
10	1.8	0.3	5.2 5.3	0.08	0.46	0.002	0.02	0.30	0.002	0.05 0.10	0.04	0.06 0.17
10	3.3	0.1	5.0	0.04	0.00	0.13	0.04	0.38	0.002	0.10	0.03	0.17
12	1.8	0.0	5.1	0.10	0.74	0.03	0.03	0.43	0.002	0.11	0.00	0.12
1	2.8	0.6	6.2	0.08	0.32	0.00	0.01	0.24	0.002	0.02	0.03	0.05
2	2.0	0.1	5.4	-0.01	0.33	0.03	0.02	0.17	0.002	0.08	0.01	0.03
3	2.5	0.5	5.8	0.05	0.47	0.05	0.01	0.28	0.02	0.23	0.003	0.02
4	6.2	0.0	5.1	-0.004	0.20	0.05	0.02	0.12	0.003	0.04	0.01	0.06
Average	4.0	0.3	5.3	0.59	0.42	0.03	0.02	0.26	0.00	0.09	0.03	0.07
Tananger (C)	$SO_2$	SO <sub>2</sub> stdv	pН	HCO <sub>3</sub> <sup>-</sup> C	$Cl^{-}$	NO <sub>3</sub> -N	$SO_4^{2-}-S$	$Na^+$	NH <sub>4</sub> <sup>+</sup> -N	$K^+$	$Mg^{2+}$	$Ca^{2+}$
5	189	136	5.4	7.4	175	0.69	7.7	94	11	3.4	11	4.3
6	7	7	5.0	100	55	0.88	2.5	27	117	6.6	3.6	1.7
7	5	0	4.8	-2.3	39	0.63	2.6	20	0.12	0.66	2.0	0.94
8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
9	203	220	4.6	20	108	0.70	4.9	62	20	5.0	8.1	3.6
10	291	409	5.2	77	224	0.43	10	127	85	8.8	15	6.1
11	701	93	8.7	63	506	1.2	26	358	0.002	16	47	27
12	1080	458	8.7	85	697	0.05	40 23	477 237	0.002	40	62 29	48 21
1 2	214 392	193 287	6.6 5.6	6.3 0.40	421 28	1.1 0.08	23 1.4	237 16	0.002 0.002	9.0 0.64	29 2.0	0.70
2 3	392 165	287 50	5.6 5.5	0.40	28 30	0.08	1.4 1.1	16	0.002	0.64	2.0 1.7	0.70
3 4	55	50 27	5.5 5.2	0.83 -0.69	30 42	0.27	1.1	22	0.03	0.98	2.5	0.89
4 Average	300	171	5.2	-0.09 357	42 211	0.15	1.8	133	21	8.3	2.3 17	10
	500	1/1	5.9	337	114	0.50	11	155	41	0.0	17	10

fine water droplets. The variation in the environments between the stations clearly dominated the smaller effects on the corrosion of the spraying with MEA.

### 5. Conclusion

The application of amine solutions to carbon steel and copper samples in the laboratory and to steel samples outdoors, resulted in reduced weight gain due to corrosion and ultimate weight reduction at high amine doses. Moderate amine exposure was found to initially inhibit the corrosion of steel, but at the same time reduce the amount and protection effect of the corrosion layer, which could in turn increase the corrosion rate. At high doses, the amine was observed to dissolve the metal without the establishing of a corrosion layer. These effects seemed much more pronounced on copper than on steel. The amines seemed to form of a corrosion inhibiting surface film, and/or reduce the surface acidity also induced by the presence of SO<sub>2</sub>, and thus the corrosion potential, and/or the dissolve the corrosion and/or the metal substrate, with increasingly more of the later effects at higher doses and pH. The reason for the dissolution of copper when it was sprayed with a high DEA dose may have been the formation of a soluble and off running Cuamine, and possibly sulphur, containing complex at the high pH

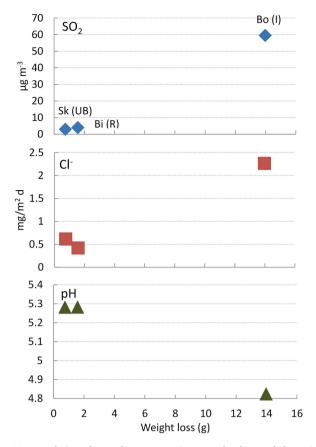


Fig. 13. Correlation of annual average environmental values and the weight loss of the samples after stripping for three stations.

(10.7) of the amine solution. Annual climate and air quality variations in Norway affect the corrosion of carbon steel much more than is expected from an annual MEA load representing 65 years of maximum modelled deposition due to emissions from a carbon capture plant.

### Data availability

The data are available in the paper and Appendix. The data files reported from the laboratory analysis that support the findings of this study are available from the corresponding author, TG, teg@nilu.no, upon reasonable request, with the permission of NILU-Norwegian Institute for Air Research.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix

Table A1.

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