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Boulder, Colorado, USA

Practice of Amine Treatment on Industrial Power Plants in Japan

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Amine Application for Feedwater Treatment in Japan

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Industrial Plants

Factory Steam Generation Plants (low pressure, no turbine)
- Used in most of units

Industrial Power Plants (turbine equipped)
- Used in more than half of units

**Easy handling (low volatile solution, lower irritating to eye/nose/throat or lung)*
Prevention of ammonia attack on copper alloy/FAC on Carbon steel

Electric Power Plants (Electrical power industry)

- Not used

**Stainless steal/titanium use instead of copper alloy*
High-pH operation using ammonia

Secondary Cycles of PWRs

- Used in some units (ETA)

**ETA has been used since 1990s (after started in US PWRs).*
High-pH operation using ETA (~ 10mg/l) for constant low-Fe (< 2μg/l) operation

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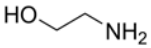
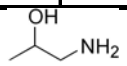
Data List (1/2)

Provided by Kurita Water Industries, Japan

Unit No.	Ammonia / Volatile Amine		Oxygen Scavenger	Const-ructor	Operation Start	Unit Type	Condensate Return	Sampling Point	Press.	Temp.
	Species	Control Target mg/l					%		MPa	℃
A	Ammonia	0.3-2.0 (pH@25℃ 9.0-9.6)	Hydrazine	MHI	2002	Conv.	98-99	Main Steam	17.0	540
B				others	2002	C.C.		LP Sat. Steam	0.4	149
								IP Sat. Steam	2.7	565
								HP Sat. Steam	12.0	568
C				others	2005			LP Sat. Steam	0.57	208
								HP Sat. Steam	7.51	514
D	Ethanolamine (ETA)	2 (9.3)		others	2003	Conv.		Main Steam	6.1	405
E	Isopropanolamine	3 (9.4)		MHI	1975	Conv.		Sat. Steam	12.0	515
F	Morpholine	15-30 (9.2-9.4)		others	1999	C.C.		LP Sat. Steam	2.0	215
								HP Sat. Steam	6.2	510
G		20 (9.3)		others	2004			LP Sat. Steam	0.5	221
								HP Sat. Steam	4.6	403
H	Isopropanolamine	1.5 (9.1)		others	2004	Conv.		Main Steam	14.7	569
	Morpholine	15 (9.2)								
	Ammonia	0.5 (9.1)								
I	Morpholine	4-5 (9.1)		others	2004	C.C.	60-80	LP Sat. Steam	0.5	185
								HP Sat. Steam	9.3	502
J	Isopropanolamine	1 (9.0)	(Organic)	MHI	1960	Conv.	52	Main Steam	12.3	538

Ammonia $pK_b = 4.76$ M.W. = 17.03 NH_3

ETA $pK_b = 4.59$ M.W. = 61.09 

Isopropanolamine $pK_b = 4.29$ M.W. = 75.11 

Morpholine $pK_b = 5.68$ M.W. = 87.12

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Data List (2/2)

Provided by Kurita Water Industries, Japan

Unit No.	Ammonia / Volatile Amine		Oxygen Scavenger	Steam (after cation resin)					Steam		Make-up Water
	Species	Control Target		C.Cond.	HCOO	CH_3COO	TOC	IC	TOC	NH_4	TOC
		mg/l		μS/cm	mg/l	mg/l	mgC/l	mgC/l	mgC/l	mg/l	mgC/l
A	Ammonia	0.3-2.0 (pH@25℃ 9.0-9.6)		0.24	—	—	0.016	0.006	—	—	0.072
B				0.21	—	—	0.070	0.005	—	—	0.200
				0.35	—	—	0.090	0.007	—	—	
				0.31	—	—	0.090	0.007	—	—	
C				—	—	—	—	—	—	—	-
				0.23	—	—	0.031	0.005	—	—	
D	Ethanolamine (ETA)	2 (9.3)		0.33	—	—	0.185	0.013	—	—	0.120
E	Isopropanolamine	3 (9.4)		0.8～1.0	<0.01	0.11	—	—	1.450	—	0.022-0.1
F	Morpholine	15-30 (9.2-9.4)	Hydrazine	—	—	—	—	—	—	—	-
				0.68	—	—	0.125	0.048	—	—	
G		20 (9.3)		1.05	—	—	0.345	0.100	—	—	0.354
				0.35	—	—	0.101	0.010	—	—	
H	Isopropanolamine	1.5 (9.1)		2.78	—	—	0.424	0.019	—	—	0.280 -0.340
	Morpholine	15 (9.2)		0.63	—	—	0.140	—	—	—	
	Ammonia	0.5 (9.1)		0.41	—	—	0.057	—	—	—	
I	Morpholine	4-5 (9.1)		0.46	0.2	0.2	0.077	0.072	—	0.300	-
				0.71	<0.1	<0.1	0.130	0.080	—	0.300	
J	Isopropanolamine	1 (9.0)	(Organic)	—	0.5	0.7	—	—	0.450	0.100	0.044-0.1

There is no turbine corrosion failure

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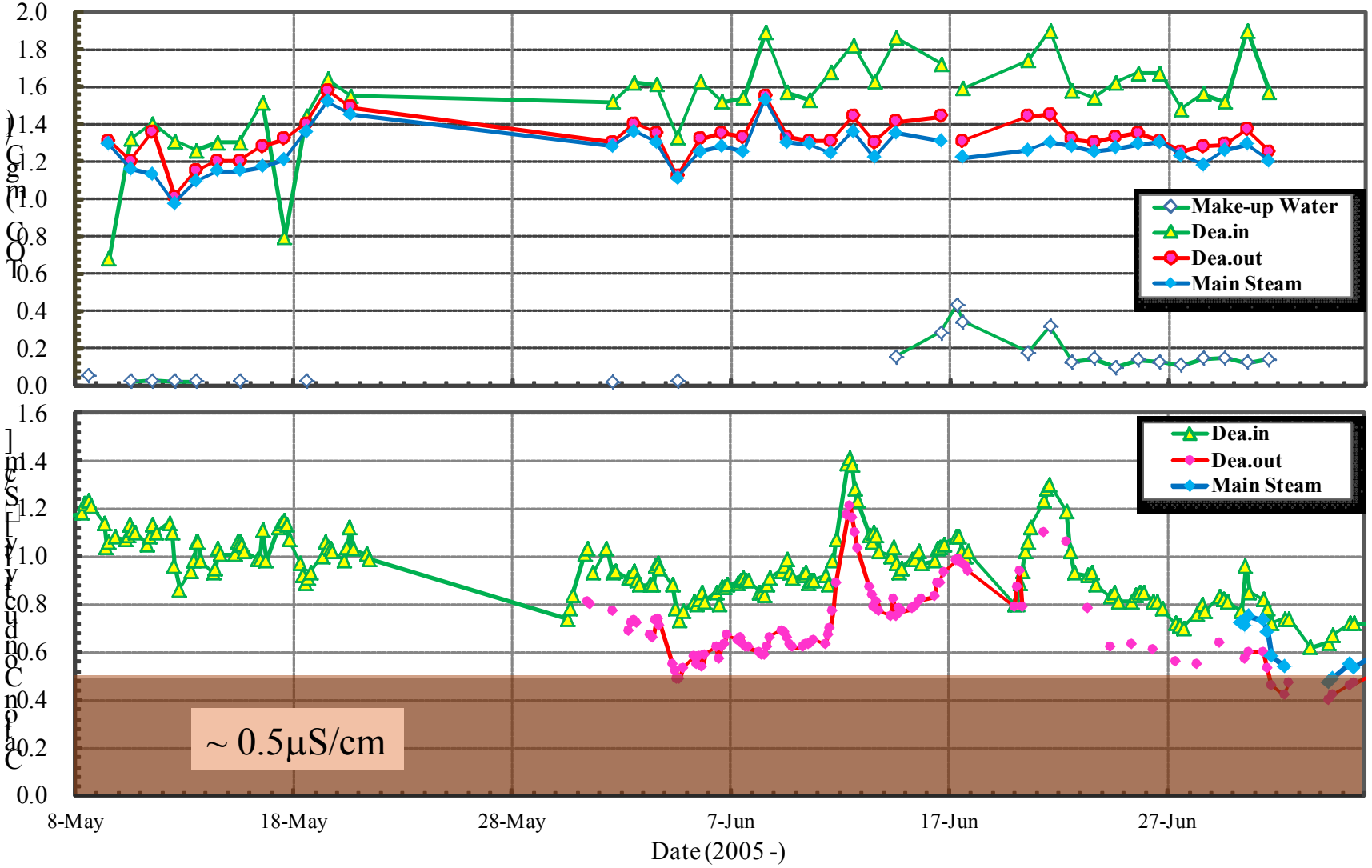
Water Analysis Data of Unit-E (on Test Operation Containing Cleanup)



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Theoretical Cation Conductivity@25C [μS/cm] of CO_3 - Cl - HCOO - CH_3COO Mixtures (1/6)

CO_3 = 0 mg/l Cl = 0 mg/l

~ 0.2 □S/cm ~ 0.5 □S/cm ~ 1.0 □S/cm 1.0 □S/cm ~

		CH_3COO [mg/l]										
		0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
HCOO [mg/l]	0	0.055	0.091	0.145	0.204	0.263	0.323	0.382	0.440	0.498	0.555	0.611
	0.01	0.111	0.168	0.228	0.288	0.348	0.407	0.466	0.524	0.581	0.638	0.693
	0.02	0.191	0.252	0.313	0.373	0.433	0.492	0.550	0.608	0.664	0.720	0.776
	0.03	0.277	0.338	0.399	0.459	0.518	0.577	0.635	0.692	0.748	0.803	0.858
	0.04	0.364	0.425	0.486	0.545	0.604	0.662	0.719	0.775	0.831	0.886	0.940
	0.05	0.452	0.512	0.572	0.631	0.689	0.747	0.803	0.859	0.914	0.968	1.022
	0.06	0.540	0.600	0.659	0.717	0.775	0.832	0.888	0.943	0.997	1.051	1.104
	0.07	0.627	0.687	0.745	0.803	0.860	0.916	0.972	1.026	1.080	1.133	1.186
	0.08	0.715	0.774	0.832	0.889	0.945	1.001	1.056	1.110	1.163	1.216	1.268
	0.09	0.803	0.861	0.918	0.975	1.031	1.085	1.140	1.193	1.246	1.298	1.350
	0.10	0.891	0.948	1.005	1.060	1.116	1.170	1.224	1.277	1.329	1.381	1.432

pK_w = 13.997

pKa (CH_3COOH) = 4.76 λ^{∞} (CH_3COO^-) = 4.09 mS・ m^2 / mol

pKa (HCOOH) = 3.75 λ^{∞} ($HCOO^-$) = 5.46

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Theoretical Cation Conductivity@25C [μS/cm] of CO_3 - Cl - HCOO - CH_3COO Mixtures (2/6)

CO_3 = 0.05 mg/l Cl = 0 mg/l

~ 0.2 □S/cm ~ 0.5 □S/cm ~ 1.0 □S/cm 1.0 □S/cm ~

HCOO [mg/l]	CH_3COO [mg/l] 0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
0	0.208	0.253	0.300	0.349	0.399	0.449	0.499	0.550	0.601	0.652	0.703
0.01	0.273	0.321	0.371	0.421	0.472	0.523	0.574	0.625	0.677	0.728	0.779
0.02	0.342	0.392	0.443	0.495	0.546	0.598	0.650	0.702	0.753	0.805	0.856
0.03	0.415	0.466	0.518	0.571	0.623	0.675	0.727	0.779	0.831	0.882	0.933
0.04	0.490	0.542	0.595	0.648	0.701	0.753	0.805	0.857	0.909	0.960	1.011
0.05	0.567	0.620	0.673	0.726	0.779	0.832	0.884	0.936	0.987	1.038	1.089
0.06	0.645	0.699	0.753	0.806	0.859	0.911	0.963	1.015	1.066	1.117	1.168
0.07	0.725	0.779	0.833	0.886	0.939	0.991	1.043	1.095	1.146	1.196	1.247
0.08	0.806	0.860	0.913	0.967	1.019	1.071	1.123	1.175	1.225	1.276	1.326
0.09	0.888	0.941	0.995	1.048	1.100	1.152	1.204	1.255	1.305	1.355	1.405
0.10	0.970	1.023	1.077	1.129	1.181	1.233	1.284	1.335	1.385	1.435	1.484

pK_w = 13.997

pKa (CH_3COOH) = 4.76
pKa (HCOOH) = 3.75
pKa (H_2CO_3) = 6.11
pKa (HCO_3^-) = 9.87

λ^∞ (CH_3COO^-) = 4.09 mS・ m^2 / mol
λ^∞ ($HCOO^-$) = 5.46
λ^∞ (HCO_3^-) = 4.45
λ^∞ (1/2 CO_3^{2-}) = 6.93

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Theoretical Cation Conductivity@25C [μS/cm] of CO_3 - Cl - HCOO - CH_3COO Mixtures (3/6)

CO_3 = 0.1 mg/l Cl = 0 mg/l

~ 0.2 □S/cm ~ 0.5 □S/cm ~ 1.0 □S/cm 1.0 □S/cm ~

		CH_3COO [mg/l]										
		0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
HCOO [mg/l]	0	0.326	0.368	0.411	0.455	0.501	0.546	0.593	0.640	0.687	0.734	0.781
	0.01	0.387	0.431	0.476	0.522	0.568	0.615	0.663	0.710	0.758	0.806	0.853
	0.02	0.451	0.497	0.544	0.591	0.638	0.686	0.734	0.782	0.830	0.878	0.927
	0.03	0.519	0.566	0.613	0.661	0.710	0.758	0.807	0.855	0.904	0.952	1.001
	0.04	0.588	0.636	0.685	0.734	0.783	0.832	0.881	0.930	0.978	1.027	1.075
	0.05	0.660	0.709	0.758	0.808	0.857	0.906	0.956	1.005	1.054	1.102	1.151
	0.06	0.733	0.783	0.833	0.883	0.932	0.982	1.031	1.081	1.129	1.178	1.226
	0.07	0.808	0.859	0.909	0.959	1.009	1.059	1.108	1.157	1.206	1.255	1.303
	0.08	0.885	0.935	0.986	1.036	1.086	1.136	1.185	1.234	1.283	1.331	1.380
	0.09	0.962	1.013	1.063	1.114	1.164	1.213	1.263	1.312	1.360	1.409	1.457
	0.10	1.040	1.091	1.142	1.192	1.242	1.292	1.341	1.390	1.438	1.486	1.534

pK_w = 13.997

pKa (CH_3COOH) = 4.76
pKa (HCOOH) = 3.75
pKa (H_2CO_3) = 6.11
pKa (HCO_3^-) = 9.87

λ^∞ (CH_3COO^-) = 4.09 mS・ m^2 / mol
λ^∞ ($HCOO^-$) = 5.46
λ^∞ (HCO_3^-) = 4.45
λ^∞ (1/2 CO_3^{2-}) = 6.93

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Theoretical Cation Conductivity@25C [μS/cm] of CO_3 - Cl - HCOO - CH_3COO Mixtures (4/6)

CO_3 = 0 mg/l Cl = 0.02 mg/l ~ 0.2 □S/cm ~ 0.5 □S/cm ~ 1.0 □S/cm 1.0 □S/cm ~

		CH_3COO [mg/l]										
		0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
HCOO [mg/l]	0	0.250	0.312	0.373	0.433	0.493	0.552	0.610	0.667	0.724	0.780	0.835
	0.01	0.337	0.399	0.459	0.519	0.579	0.637	0.694	0.751	0.807	0.862	0.917
	0.02	0.425	0.486	0.546	0.606	0.664	0.722	0.779	0.835	0.891	0.945	0.999
	0.03	0.513	0.573	0.633	0.692	0.750	0.807	0.864	0.919	0.974	1.028	1.082
	0.04	0.601	0.661	0.720	0.778	0.836	0.892	0.948	1.003	1.057	1.111	1.164
	0.05	0.689	0.748	0.807	0.864	0.921	0.977	1.032	1.087	1.141	1.194	1.246
	0.06	0.777	0.836	0.894	0.951	1.007	1.062	1.117	1.171	1.224	1.276	1.328
	0.07	0.865	0.923	0.980	1.036	1.092	1.147	1.201	1.254	1.307	1.359	1.410
	0.08	0.953	1.010	1.067	1.122	1.177	1.231	1.285	1.338	1.390	1.441	1.492
	0.09	1.040	1.097	1.153	1.208	1.262	1.316	1.369	1.421	1.473	1.524	1.574
	0.10	1.128	1.184	1.239	1.293	1.347	1.400	1.453	1.504	1.556	1.606	1.656

pK_w = 13.997

pKa (CH_3COOH) = 4.76 λ^{∞} (CH_3COO^-) = 4.09 mS・ m^2 / mol

pKa (HCOOH) = 3.75 λ^{∞} ($HCOO^-$) = 5.46

pKa (HCl) = -3.7 λ^{∞} (Cl^-) = 7.631

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Theoretical Cation Conductivity@25C [μS/cm] of CO_3 - Cl - HCOO - CH_3COO Mixtures (5/6)

CO_3 = 0.05 mg/l Cl = 0.02 mg/l

~ 0.2 □S/cm ~ 0.5 □S/cm ~ 1.0 □S/cm 1.0 □S/cm ~

		CH_3COO [mg/l]										
		0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
HCOO [mg/l]	0	0.394	0.445	0.497	0.549	0.601	0.654	0.706	0.758	0.809	0.861	0.912
	0.01	0.469	0.521	0.573	0.626	0.679	0.731	0.784	0.836	0.887	0.939	0.990
	0.02	0.545	0.598	0.651	0.704	0.757	0.810	0.862	0.914	0.966	1.017	1.068
	0.03	0.623	0.677	0.730	0.784	0.837	0.889	0.942	0.994	1.045	1.096	1.147
	0.04	0.703	0.757	0.810	0.864	0.917	0.969	1.021	1.073	1.125	1.175	1.226
	0.05	0.783	0.837	0.891	0.944	0.997	1.050	1.102	1.153	1.204	1.255	1.305
	0.06	0.865	0.919	0.972	1.025	1.078	1.130	1.182	1.234	1.284	1.335	1.385
	0.07	0.947	1.001	1.054	1.107	1.160	1.212	1.263	1.314	1.365	1.415	1.464
	0.08	1.029	1.083	1.136	1.189	1.241	1.293	1.344	1.395	1.445	1.495	1.544
	0.09	1.112	1.166	1.219	1.271	1.323	1.374	1.425	1.476	1.525	1.575	1.624
	0.10	1.196	1.249	1.301	1.354	1.405	1.456	1.507	1.557	1.606	1.655	1.704

pK_w = 13.997

pKa (CH_3COOH) = 4.76
pKa (HCOOH) = 3.75
pKa (H_2CO_3) = 6.11
pKa (HCO_3^-) = 9.87
pKa (HCl) = -3.7

λ^∞ (CH_3COO^-) = 4.09 mS・ m^2 / mol
λ^∞ ($HCOO^-$) = 5.46
λ^∞ (HCO_3^-) = 4.45
λ^∞ (1/2 CO_3^{2-}) = 6.93
λ^∞ (Cl^-) = 7.631

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Theoretical Cation Conductivity@25C [μS/cm] of CO_3 - Cl - HCOO - CH_3COO Mixtures (6/6)

CO_3 = 0.1 mg/l Cl = 0.02 mg/l

~ 0.2 □S/cm ~ 0.5 □S/cm ~ 1.0 □S/cm 1.0 □S/cm ~

		CH_3COO [mg/l]										
		0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
HCOO [mg/l]	0	0.501	0.547	0.595	0.642	0.691	0.739	0.787	0.836	0.884	0.933	0.981
	0.01	0.569	0.617	0.666	0.714	0.763	0.812	0.861	0.910	0.959	1.007	1.056
	0.02	0.640	0.689	0.738	0.788	0.837	0.886	0.936	0.985	1.034	1.083	1.131
	0.03	0.713	0.763	0.813	0.863	0.912	0.962	1.011	1.061	1.110	1.158	1.207
	0.04	0.788	0.838	0.888	0.939	0.988	1.038	1.088	1.137	1.186	1.235	1.283
	0.05	0.864	0.915	0.965	1.015	1.066	1.115	1.165	1.214	1.263	1.312	1.360
	0.06	0.941	0.992	1.043	1.093	1.143	1.193	1.243	1.292	1.341	1.389	1.437
	0.07	1.019	1.070	1.121	1.171	1.222	1.271	1.321	1.370	1.419	1.467	1.515
	0.08	1.098	1.149	1.200	1.250	1.300	1.350	1.399	1.448	1.497	1.545	1.593
	0.09	1.178	1.229	1.280	1.330	1.380	1.429	1.478	1.527	1.575	1.623	1.671
	0.10	1.258	1.309	1.360	1.410	1.459	1.509	1.557	1.606	1.654	1.702	1.749

pK_w = 13.997

pKa (CH_3COOH) = 4.76
pKa (HCOOH) = 3.75
pKa (H_2CO_3) = 6.11
pKa (HCO_3^-) = 9.87
pKa (HCl) = -3.7

λ^∞ (CH_3COO^-) = 4.09 mS・ m^2 / mol
λ^∞ ($HCOO^-$) = 5.46
λ^∞ (HCO_3^-) = 4.45
λ^∞ (1/2 CO_3^{2-}) = 6.93
λ^∞ (Cl^-) = 7.631

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Theoretical Cation Conductivity@25C [μS/cm] of CO_3 - Cl - HCOO - CH_3COO – SO_4 Mixtures (1/2)

CO_3 = 0 mg/l

HCOO = 0 mg/l

CH_3COO = 0 mg/l

~ 0.2 □S/cm | ~ 0.5 □S/cm | ~ 1.0 □S/cm | 1.0 □S/cm ~

Cl [mg/l]	SO_4 [mg/l] 0	0.002	0.004	0.006	0.008	0.01	0.012	0.014	0.016	0.018	0.02
0	0.055	0.063	0.073	0.084	0.098	0.112	0.127	0.142	0.159	0.175	0.192
0.002	0.066	0.076	0.089	0.102	0.117	0.132	0.148	0.164	0.181	0.197	0.214
0.004	0.080	0.093	0.107	0.122	0.137	0.153	0.170	0.186	0.203	0.220	0.237
0.006	0.098	0.112	0.127	0.143	0.159	0.175	0.192	0.209	0.226	0.243	0.260
0.008	0.117	0.133	0.148	0.165	0.181	0.198	0.215	0.232	0.249	0.266	0.284
0.01	0.138	0.154	0.170	0.187	0.204	0.221	0.238	0.255	0.272	0.290	0.307
0.012	0.159	0.176	0.193	0.209	0.227	0.244	0.261	0.278	0.296	0.313	0.331
0.014	0.182	0.198	0.215	0.232	0.250	0.267	0.284	0.302	0.319	0.337	0.354
0.016	0.204	0.221	0.238	0.256	0.273	0.290	0.308	0.325	0.343	0.360	0.378
0.018	0.227	0.244	0.261	0.279	0.296	0.314	0.331	0.349	0.366	0.384	0.401
0.02	0.250	0.267	0.285	0.302	0.320	0.337	0.355	0.372	0.390	0.408	0.425

pK_w = 13.997

pKa (H_2SO_4) = -5.00

pKa (HSO_4^-) = 1.99

λ^∞ (HSO_4^-) = 5.00

λ^∞ (1/2 SO_4^{2-}) = 8.00

pKa (HCl) = -3.7

λ^∞ (Cl^-) = 7.631 mS・ m^2 / mol

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Theoretical Cation Conductivity@25C [μS/cm] of CO_3 - Cl - HCOO - CH_3COO – SO_4 Mixtures (2/2)

CO_3 = 0.05 mg/l CH_3COO = 0.03 mg/l ~ 0.2 □S/cm ~ 0.5 □S/cm ~ 1.0 □S/cm 1.0 □S/cm ~

HCOO = 0.02 mg/l

Cl [mg/l]	SO_4 [mg/l] 0	0.002	0.004	0.006	0.008	0.01	0.012	0.014	0.016	0.018	0.02
0	0.495	0.510	0.525	0.541	0.556	0.572	0.587	0.603	0.619	0.634	0.650
0.002	0.515	0.531	0.546	0.561	0.577	0.593	0.608	0.624	0.640	0.655	0.671
0.004	0.536	0.551	0.567	0.582	0.598	0.614	0.629	0.645	0.661	0.677	0.693
0.006	0.557	0.572	0.588	0.603	0.619	0.635	0.650	0.666	0.682	0.698	0.714
0.008	0.577	0.593	0.609	0.624	0.640	0.656	0.672	0.688	0.704	0.719	0.736
0.01	0.598	0.614	0.630	0.645	0.661	0.677	0.693	0.709	0.725	0.741	0.757
0.012	0.619	0.635	0.651	0.667	0.683	0.698	0.714	0.730	0.746	0.763	0.779
0.014	0.640	0.656	0.672	0.688	0.704	0.720	0.736	0.752	0.768	0.784	0.800
0.016	0.662	0.678	0.693	0.709	0.725	0.741	0.757	0.774	0.790	0.806	0.822
0.018	0.683	0.699	0.715	0.731	0.747	0.763	0.779	0.795	0.811	0.828	0.844
0.02	0.704	0.720	0.736	0.752	0.769	0.785	0.801	0.817	0.833	0.850	0.866

pK_w = 13.997
pKa (H_2SO_4) = -5.00
pKa (HSO_4^-) = 1.99
λ^∞ (HSO_4^-) = 5.00
λ^∞ (1/2 SO_4^{2-}) = 8.00

pKa (CH_3COOH) = 4.76
pKa (HCOOH) = 3.75
pKa (H_2CO_3) = 6.11
pKa (HCO_3^-) = 9.87
pKa (HCl) = -3.7

λ^∞ (CH_3COO^-) = 4.09 mS・ m^2 / mol
λ^∞ ($HCOO^-$) = 5.46
λ^∞ (HCO_3^-) = 4.45
λ^∞ (1/2 CO_3^{2-}) = 6.93
λ^∞ (Cl^-) = 7.631

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Conclusion

Idea for Guidance of Cation Conductivity Monitoring on Steam for Amine Treatment

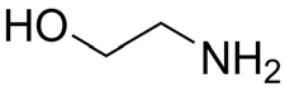
Experimental idea for cost-effective operation :

- Normal value("N-limit" in VGB) should be set less than or equal to 0.5 μS/cm.
- Weekly analysis of Cl/SO_4 on drum water
  - Keeping lower than (3 / blowdown rate) μg/l respectively
    (Example : blowdown rate = 1% □ < 300 μg/l Cl, < 300 μg/l SO_4
- Exceeding the value of (N-limit + 0.2) μS/cm means that the risk of corrosion-related failures is getting higher.

Questions for Guideline Formulation

- Clarifying decomposition characteristics of each amines
- Key Instrumentation for decomposition product determination
  - Degassed cation conductivity, Ion chromatography … *cost-effective?*

*ETA(Ethanolamine) must be targeted to start because



- Enough experiences in PWRs
- Simple decomposition characteristic
  - CO_2, NH_3, HCOOH, CH_3COOH, $CH_2OHCOOH$

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