

● Pulp and Paper Technical Association of Canada

● BLEACHING COMMITTEE FALL 2019

- GRAND PACIFIC, VICTORIA, BC

● BLEACH TOWER MORTAR TESTING

- Resistance to Chlorine Dioxide

- **Author: Robert Gallant**

- President TAC West Ltd.
- Vice-President TAC Inc

- | | |
|--------------------|--------------------------|
| ● TAC Inc. | TAC West LTD |
| ● Montreal, Quebec | Quesnel British Columbia |
| ● (514) 737-8566 | (250) 992-9336 |



Bleach Towers

D0,D1 & D2

Objective:

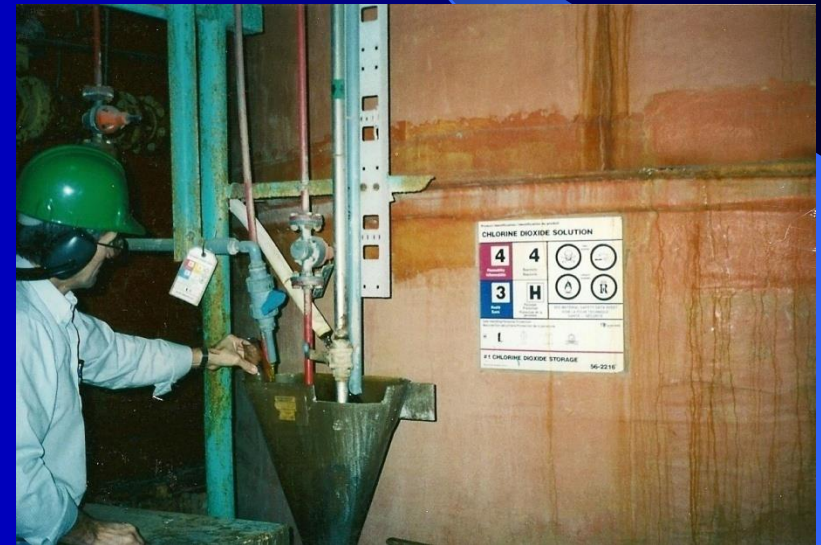
- Research the after-performance life cycles of post-repointing work in Bleach Towers.
- Determine what Mortars are most chemically resistant in ClO_2 environment.
- Measure the weight loss as a function of its Initial cure to corrosion within Kraft Bleaching.

Testing Procedures

- Seven types of mortar were furnished by suppliers. Samples tested were fully cured with mix-ratios monitored under ideal lab conditions for trials 1, 2 and 3, the fourth trial was mixed and cured on site for 6hr, 12hr and 24hr before immersion in ClO_2 solution.
- Testing was carried out in two Kraft Pulp Mills over a period of five years.
- Different immersion tests were completed using strong concentrations 10-12 g/l ClO_2 solution at different temperatures, ranging from ambient 70° F to simulated bleach operating conditions of 180° F
- ClO_2 solution was changed @ 2.5 days intervals to maintain it's strength over a period of 90 days or to failure which was found to be 41 cycles approx. 100 days.
- 1140 research hours has been invested to date.

Trial 1 $T = 70^{\circ} F$

1" dia. x 1" H cylinders of mortar was furnished by three manufacturers



Trial 1

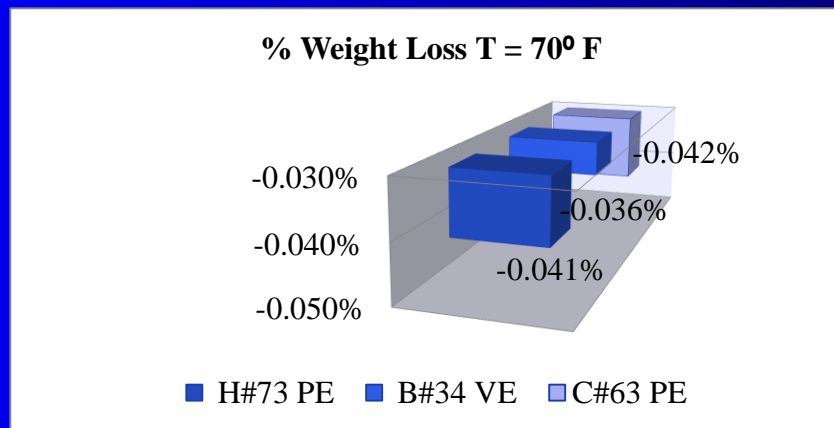
End of trial 90 days. 3 cylinders / vessel (not shown)



Trial 1 Supplier A T = 70° F

Conclusion: Minimal weight loss, although VE showed a 12% less wt. loss than PE

	H#73 PE			B#34 VE			C#63 PE	
	Before	After		Before	After		Before	After
BOTTOM	24.9570	24.9475		25.3016	25.2921		24.5586	24.547
MIDDLE	24.9568	24.9465		25.3085	25.2986		24.5534	24.544
TOP	24.9464	24.9356		25.3099	25.3022		24.5457	24.536
Average Wt.	24.9534	24.9432		25.3067	25.2976		24.5526	24.5423
Wt. Loss		-0.01			-0.01			-0.01
% Wt. Loss		-0.041%			-0.036%			-0.042%

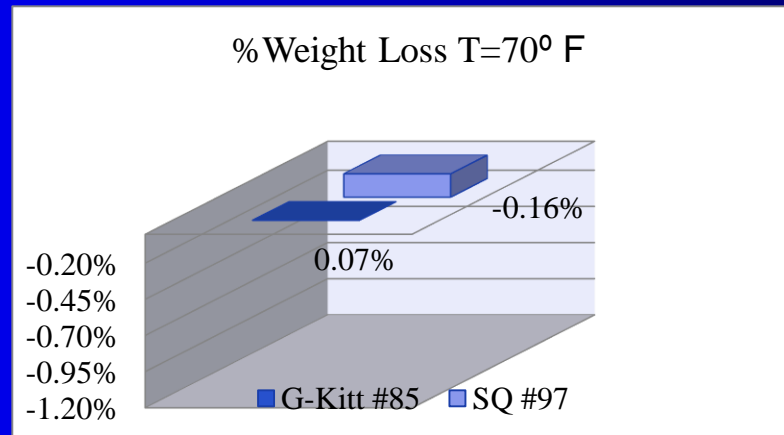


Trial 1 Supplier D T = 70° F

Conclusion: Slight wt. gain with VE & wt loss of .16%
with PE

Note: 128% diff !

	G-Kitt #85		SQ #97	
	BEFORE	AFTER	BEFORE	AFTER
BOTTOM	19.6173	19.6322	25.1881	25.0554
MIDDLE	21.5656	21.5776	24.2882	24.2893
TOP	20.3425	20.3572	24.7613	24.7734
Average Wt.	20.50847	20.5223	24.7459	24.7060
Wt. Loss		0.0139		-0.0398
% Wt. Loss		0.07%		-0.16%

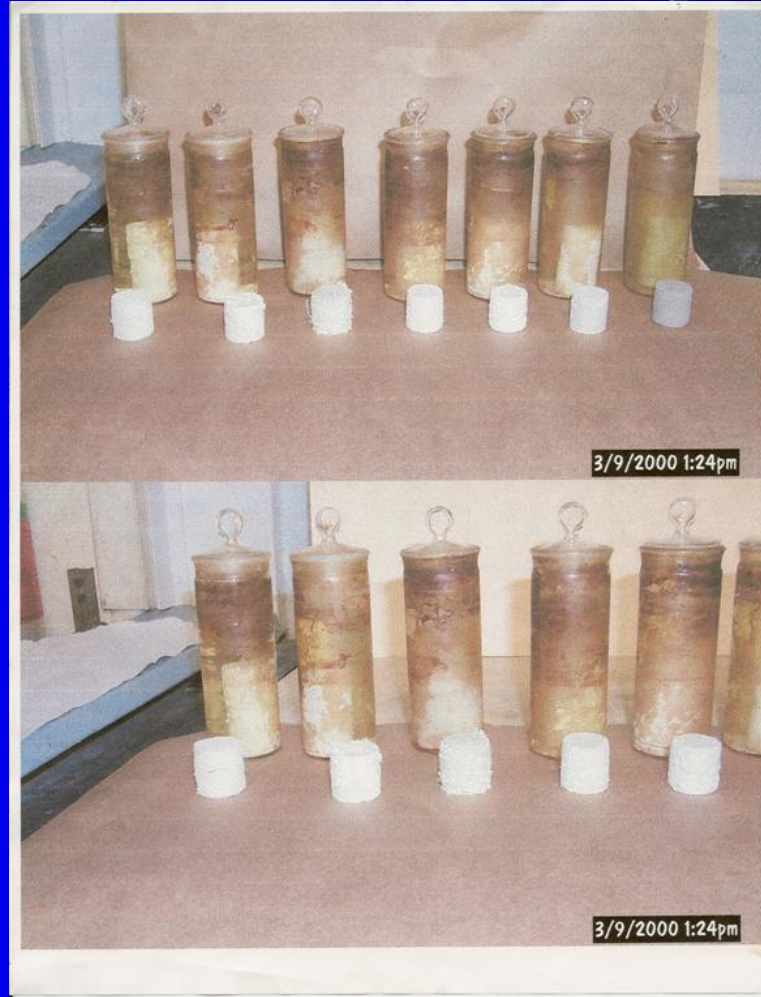


Trial 2 180° F ClO_2 @ 9.8 g/l changed every 2.5 days for 90 days

Note: plastic vessels did not hold up in ClO_2

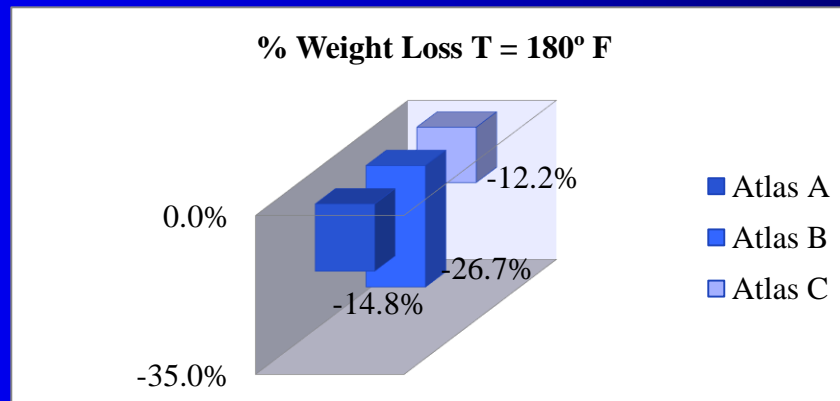


Trial 2 180° F ClO₂ @ 9.8 g/l changed every 2.5 days for 90 days



Trial 2 Supplier A 180° F ClO₂ @ 9.8 g/l changed every 2.5 days for 90 days

		Weight Before Test			Average Wt.		Wt. Loss	% wt. Loss
		Top	Middle	Bottom	Initial Total	Final Total		
Atlas Mortar A	VE	24.8108	24.8165	24.8145	74.4418	63.4235	-11.0183	-14.8%
Atlas Mortar B	PE	25.9136	25.9234	25.9174	77.7544	56.9792	-20.7752	-26.7%
Atlas Mortar C	VE	24.8642	24.8649	24.8619	74.5910	65.5128	-9.0782	-12.2%

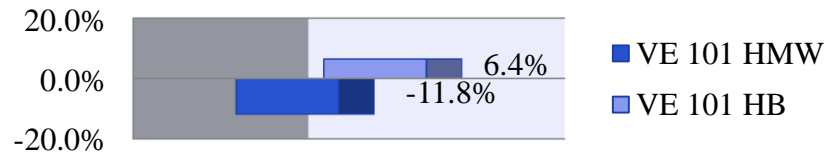


Trial 2 Supplier B 180° F ClO₂ @ 9.8 g/l changed every 2.5 days for 90 days

Note: Wt. gain +6.4% Vs. Wt. loss -11.8% for both VE

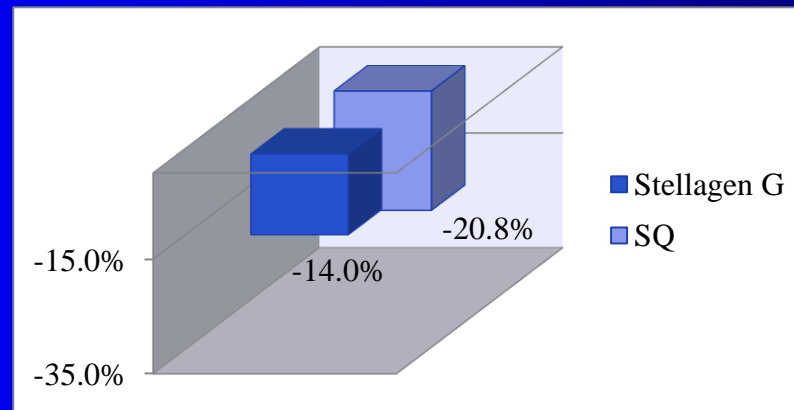
	Weight Before Test			Average Wt.		Wt. Loss	% Wt. Loss
	Top	Middle	Bottom	Initial Total	Final Total		
VE 101 HMW	22.4051	22.7370	22.3049	67.4470	59.4720	-7.975	-11.8%
VE 101 HB	20.9061	22.2357	21.2498	64.3916	68.5409	4.1493	6.4%

% Weight loss T = 180°

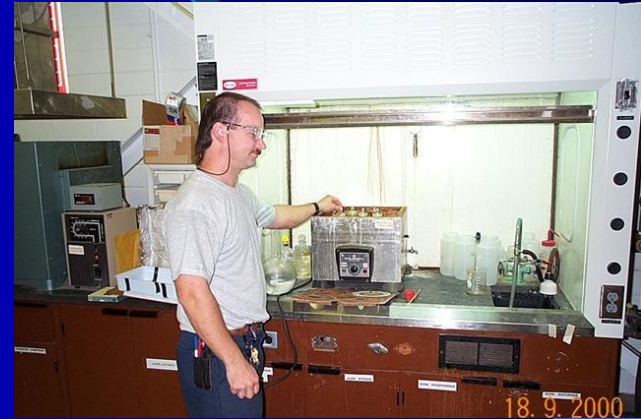


Trial 2 Supplier D 180° F ClO₂ @ 9.8 g/l changed every 2.5 days for 90 days

	Weight Before Test			Average Wt.		Wt. Loss	% Wt. Loss
	Top	Middle	Bottom	Initial Total	Final Total		
Stellagen G	26.6391	25.8728	27.2008	79.7127	68.5216	-11.1911	-14.0%
SQ	25.8411	23.7725	24.3472	73.9608	58.5925	-15.3683	-20.8%



Trial 3 180° F ClO_2 @ 11.0 g/l changed every 2.5 days & weight taken each cycle for 90 days



- Initial mass was recorded. Samples were weighed at the start and end of each cycle (2.5 days).
- Samples were placed into numbered glass vessels and filled with 10-12 g/l ClO_2 solution.
- Vessels were then placed into a hot water bath @ 180° F.

Trial 3 180° F ClO_2 @ 11.9 g/l changed every 2.5 days & weight taken for 90 days

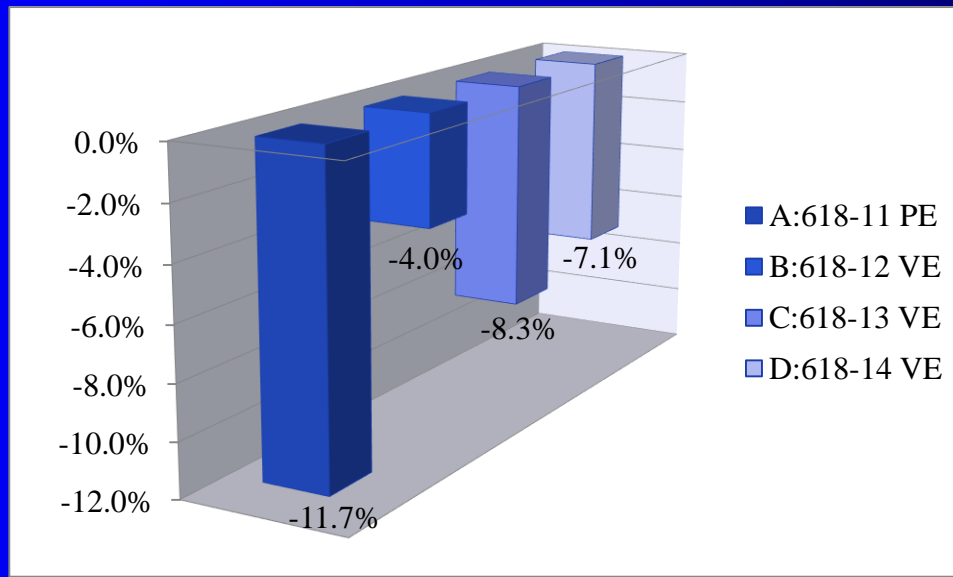


- After 2.5 days under a fume hood, samples were removed and put into a desiccator for 1 hour, so they can cool down in a 0% humidity atmosphere.
- Weight of samples were taken to see if there was significant difference in mass.

Trial 3 Supplier A 180° F ClO₂ @ 11.9 g/l changed every 2.5 days & weight taken for 90 days

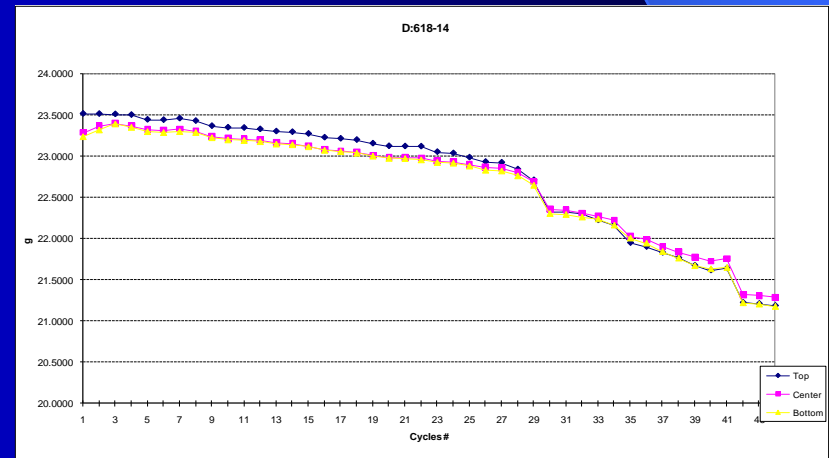
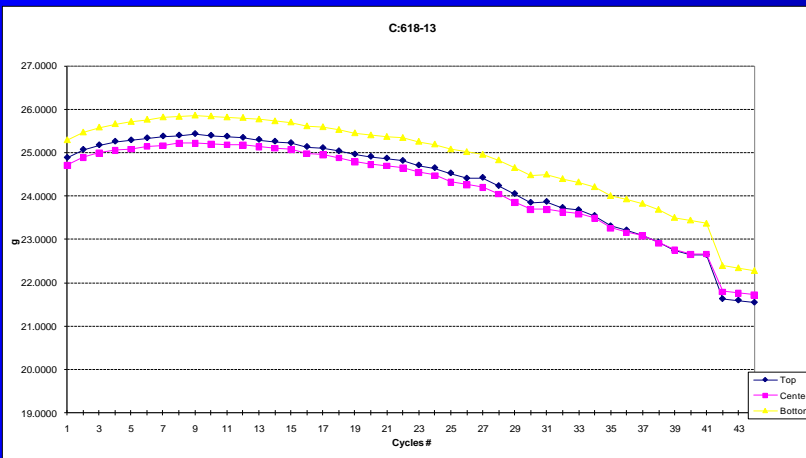
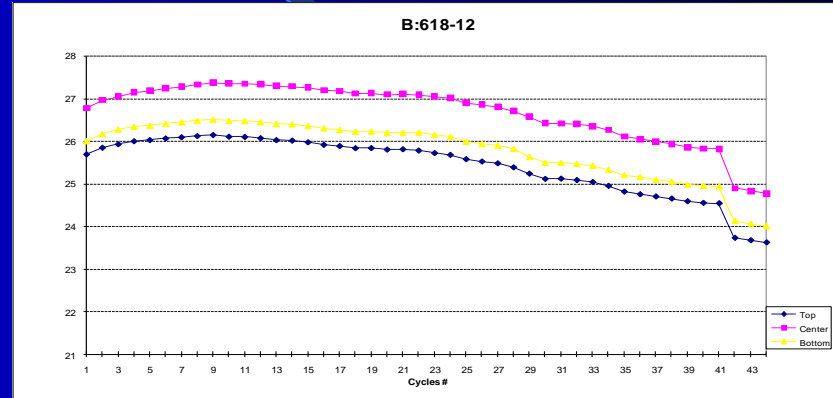
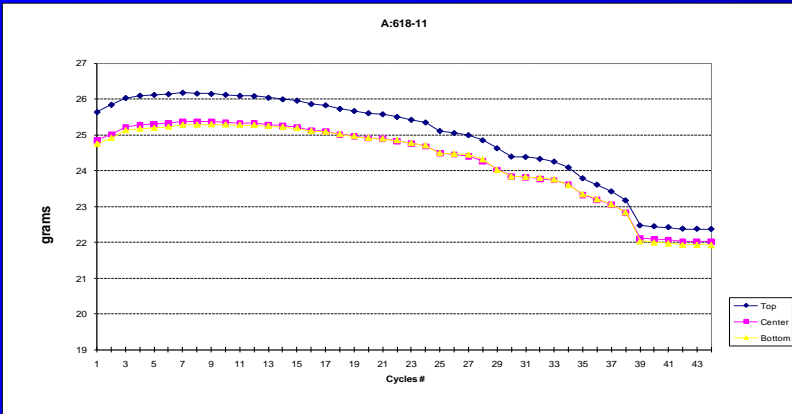
Some vinyl esters react better

	A:618-11 PE		B:618-12 VE		C:618-13 VE		D:618-14 VE	
	Before	After	Before	After	Before	After	Before	After
BOTTOM	24.7520	21.9798	25.9962	24.9395	25.2926	23.3697	23.2402	21.6491
MIDDLE	24.8532	22.0694	26.7738	25.8212	24.7200	22.6692	23.2865	21.7611
TOP	25.6374	22.4204	25.6893	24.5397	24.8858	22.6505	23.5179	21.6422
Average Wt.	25.0809	22.1565	26.1531	25.1001	24.9661	22.8965	23.3482	21.6841
Wt. Loss		-2.92		-1.05		-2.07		-1.66
% Wt. Loss		-11.7%		-4.0%		-8.3%		-7.1%



Trial 3 Supplier A 180° ClO₂ @ 11.9 g/l replaced every 2.5 days, change in weight recorded for 41 cycles

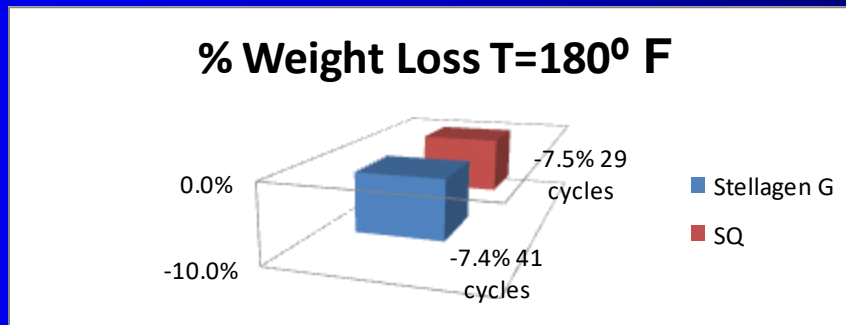
Note curve of B-618-12



Trial 3 Supplier D 180° F ClO₂ @ 11.0 g/l changed every 2.5 days & weight taken for 90 days

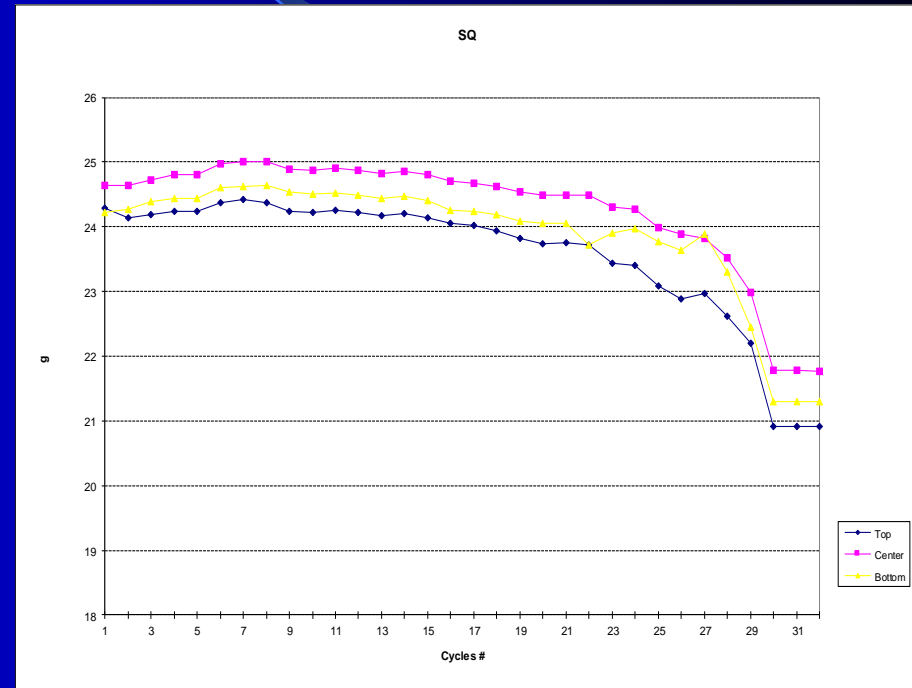
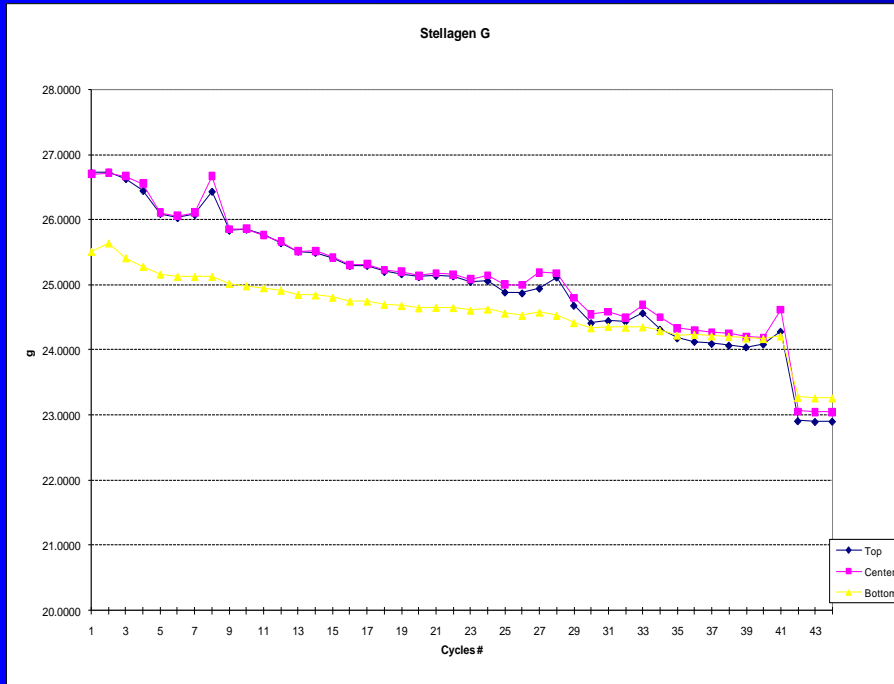
Note: SQ went to 29 cycles before failure @ -7.5% Vs 41 cycles of VE for the same % Wt. loss

	Stellagen G		SQ		
	Before	After	Before	After	
BOTTOM	25.5186	24.2157	24.2171	22.4542	
MIDDLE	26.6965	24.6221	24.6405	22.9880	
TOP	26.7217	24.2863	24.2889	22.2082	
Average Wt.	26.3123	24.3747	24.3822	22.5501	
Wt. Loss		-1.94		-1.83	(41-29) cycles
% Wt. Loss		-7.4%		-7.5%	41%



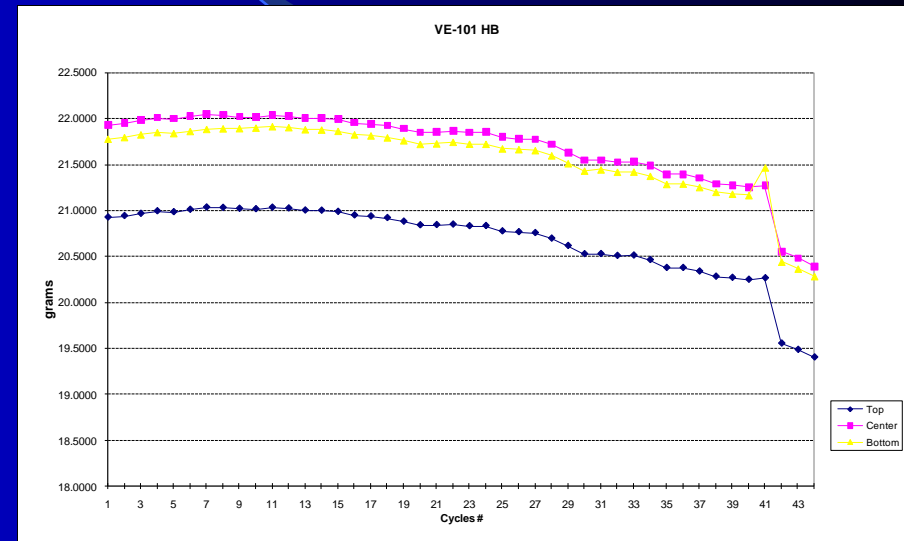
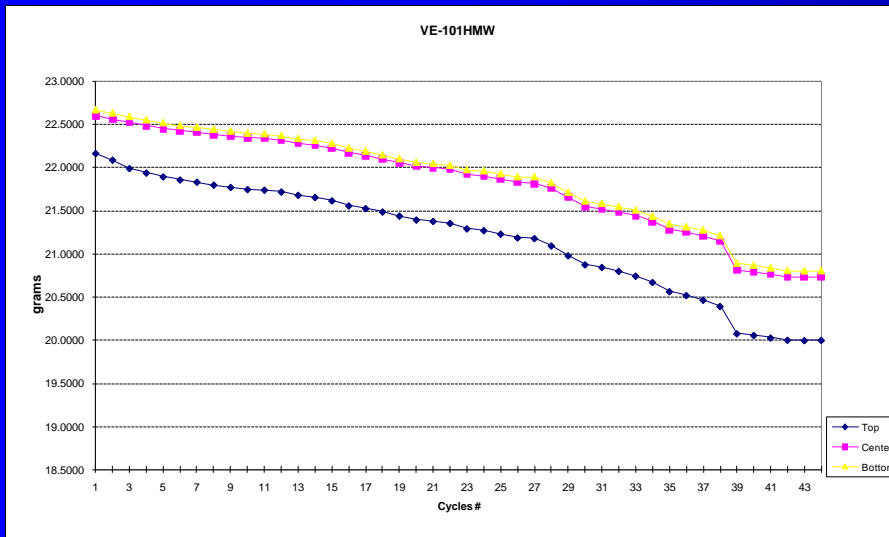
Trial 3 Supplier D ClO_2 @ 11.9 g/l replaced every 2.5 days, change in weight recorded

Note : The slope curves of 41 Vs 29 cycles



Trial 3 Supplier B ClO_2 @ 11.9 g/l replaced every 2.5 days, change in weight recorded

Note: Notice the change in slope, same cycles

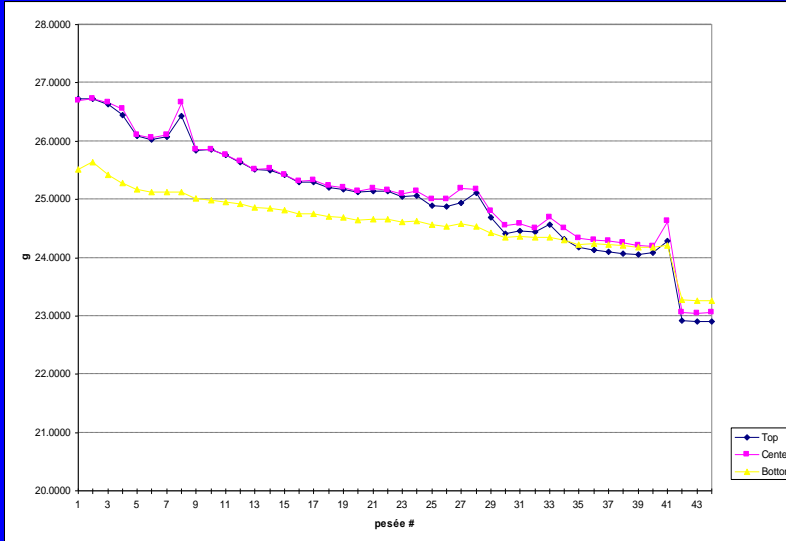


● Typical data log used to record findings

Date Entered	Time	Date Out	Time	Cycle	Top	Center	Bottom	CIO2 g/L	REMARKS
00/05/18	15:55	00/05/19	13:00	1	23.5179	23.2865	23.2402	11.9	sln claire, léger dépôt, mat en surface
00/05/19	16:00	00/05/22	9:30	2	23.5166	23.3679	23.3222	11.8	dépôt blanc, sln claire, mat blanche en surface
00/05/22	15:40	00/05/24	11:30	3	23.5125	23.4010	23.3951	11.7	sln claire, léger dépôt, mat en surface
00/05/24	14:30	00/05/26	8:00	4	23.5044	23.3730	23.3537	11.5	sln claire, léger dépôt, légère désintégration des parois
00/05/26	12:25	00/05/29	10:45	5	23.4465	23.3260	23.3016	11.9	sln claire, léger dépôt
00/05/29	16:00	00/05/31	11:50	6	23.4427	23.3187	23.2900	11.3	sln claire, léger dépôt
00/05/31	15:42	00/06/02	11:41	7	23.4607	23.3318	23.3017	12.0	sln claire, dépôt
00/06/02	15:37	00/06/05	7:30	8	23.4314	23.3079	23.2909	12.0	sln claire, léger dépôt
00/06/07	9:00	00/06/09	9:02	9	23.3697	23.2397	23.2276	11.6	sln claire, léger dépôt
00/06/09	13:00	00/06/12	10:40	10	23.3506	23.2174	23.2012	12.1	sln claire, léger dépôt
00/06/12	15:03	00/06/14	9:48	11	23.3473	23.2098	23.1939	11.9	solution jaune pâle, léger dépôt
00/06/14	15:26	00/06/16	9:17	12	23.3306	23.1946	23.1795	11.9	solution jaune pâle, léger dépôt
00/06/16	15:50	00/06/19	8:40	13	23.3040	23.1633	23.1501	11.2	solution incolore, léger dépôt
00/06/19	15:15	00/06/21	9:10	14	23.2965	23.1564	23.1425	11.6	sln claire, léger dépôt
00/06/21	15:54	00/06/24	10:55	15	23.2752	23.1286	23.1179	12.3	sln claire, léger dépôt
00/06/24	18:00	00/06/26	9:40	16	23.2297	23.0782	23.0745	12.1	Solution Claire, Léger Dépôt
00/06/27	15:35	00/06/30	8:30	17	23.2162	23.0662	23.0588	11.5	Solution Claire, Léger Dépôt
00/06/30	18:00	00/07/03	9:40	18	23.2011	23.0503	23.0394	11.8	Solution Claire, Léger Dépôt
00/07/03	15:40	00/07/05	8:55	19	23.1571	23.0137	23.0035	12.0	Solution Jaune, Léger Dépôt
00/07/05	14:45	00/07/07	10:45	20	23.1258	22.9883	22.9769	11.2	Solution Jaune Pâle, Dépôt
00/07/10	9:25	00/07/12	9:30	21	23.1228	22.9846	22.9740	11.9	Solution Jaune, Léger Dépôt
00/07/12	14:00	00/07/14	9:35	22	23.1211	22.9798	22.9582	12.1	sln claire, dépôt
00/07/14	14:48	00/07/17	9:00	23	23.0545	22.9460	22.9260	11.5	solution incolore, léger dépôt
00/07/21	13:00	00/07/24	8:30	24	23.0384	22.9359	22.9179	11.9	solution incolore, léger dépôt
00/07/24	15:00	00/07/26	0:00	25	22.9877	22.8995	22.8824	12.0	Solution Jaune, Léger Dépôt
00/07/28	13:30	00/07/31	9:30	26	22.9342	22.8679	22.8323	12.2	solution incolore, léger dépôt
00/07/31	15:30	00/08/02	9:30	27	22.9259	22.8591	22.8231	11.9	Solution Jaune, Léger Dépôt
00/08/04	10:00	00/08/07	9:30	28	22.8432	22.8067	22.7636	11.5	
00/08/09	11:30	00/08/14	9:15	29	22.7126	22.6950	22.6488	11.6	sln claire, dépôt
00/08/15	9:53	00/08/17	9:50	30	22.3289	22.3582	22.3057	11.6	Solution incolore, dépôt
00/08/17	15:26	00/08/18	9:35	31	22.3276	22.3458	22.2937	11.7	Solution jaune, Dépôt
00/08/18	15:00	00/08/21	10:30	32	22.2997	22.3128	22.2628	11.5	Solution incolore, Dépôt
00/08/21	15:00	00/08/23	8:15	33	22.2256	22.2731	22.2398	11.9	Solution incolore, Dépôt
00/08/23	13:30	00/08/25	9:00	34	22.1707	22.2264	22.1648	11.5	Solution Jaune Pâle, Dépôt
00/08/25	15:30	00/08/28	9:06	35	21.9511	22.0286	22.0073	11.8	Solution incolore, Dépôt
00/08/29	9:00	00/08/30	9:00	36	21.9031	21.9877	21.9454	11.7	Solution jaune, Dépôt
00/08/30	15:20	00/09/01	8:50	37	21.8322	21.9056	21.8434	11.5	Solution jaune, Dépôt
00/09/01	15:45	00/09/05	6:54	38	21.7680	21.8369	21.7635	11.6	Solution incolore, Dépôt
00/09/05	11:30	00/09/07	9:40	39	21.6758	21.7779	21.6713	11.7	Solution jaune, Dépôt
00/09/07	14:45	00/09/08	9:00	40	21.6173	21.7302	21.6332	11.4	Solution jaune, Dépôt
00/09/08	15:48	00/09/11	8:45	41	21.6422	21.7611	21.6491		Solution incolore, dépôt
				42	21.2250	21.3212	21.2199		pour pesées à poids constant #1
				43	21.2118	21.3083	21.2040		pour pesées à poids constant #2
				44	21.1869	21.2872	21.1755		pour pesées à poids constant #3

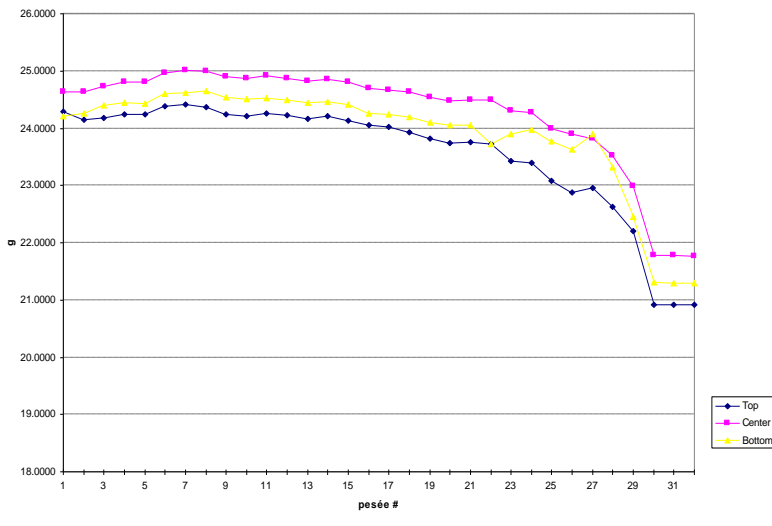
Average weight loss -1.66407 -7.1%

Interpretation of Data (41 cycles)



Immersion Testing Vinyl-Ester Sample "G"									
Date Entered	Time	Date Out	Time	Cycle	Top	Center	Bottom	CIO2 g/L	REMARKS
00/05/18	15:55	00/05/19	13:00	1	26.7217	26.6965	25.5186	11.9	léger dépôt, s/n verdâtre
00/05/19	16:00	00/05/22	9:30	2	26.7260	26.7199	25.6464	11.8	(A) s/n claire, léger dépôt
00/05/22	15:40	00/05/24	11:30	3	26.6254	26.6677	25.4187	11.7	(B) s/n claire
00/05/24	14:30	00/05/26	8:00	4	26.4440	26.5487	25.2864	11.5	(C) s/n jaune pâle
00/05/26	12:25	00/05/29	10:45	5	26.0912	26.1116	25.1678	11.9	(D) s/n claire, léger dépôt
00/05/29	16:00	00/05/31	11:50	6	26.0272	26.0617	25.1338	11.3	(E) s/n claire, léger dépôt
00/05/31	15:42	00/06/02	11:41	7	26.0759	26.1062	25.1300	12.0	(G)(H) s/n claire, léger dépôt
00/06/02	15:37	00/06/05	7:30	8	26.4314	26.6630	25.1324	12.0	(I) s/n claire, léger dépôt
00/06/07	9:00	00/06/09	9:02	9	25.8352	25.8573	25.0247	11.6	(K) (L) s/n jaune pâle, léger dépôt
00/06/09	13:00	00/06/12	10:40	10	25.8501	25.8579	24.9866	12.1	(M) s/n claire, léger dépôt
00/06/12	15:03	00/06/14	9:48	11	25.7657	25.7664	24.9580	11.9	(N) Solution jaune, léger dépôt
00/06/14	15:26	00/06/16	9:17	12	25.6425	25.6621	24.9199	11.9	(O) Solution jaune, léger dépôt
00/06/16	15:50	00/06/19	8:40	13	25.5129	25.5218	24.8549	11.2	(P) Solution jaune très pâle, léger dépôt
00/06/19	15:15	00/06/21	9:10	14	25.4961	25.5229	24.8469	11.6	(Q) s/n jaune pâle, léger dépôt
00/06/21	15:54	00/06/24	10:55	15	25.4139	25.4242	24.8109	12.3	(R) s/n clair, léger dépôt
00/06/24	18:00	00/06/26	9:40	16	25.2947	25.3099	24.7524	12.1	(S) Solution jaune pâle, Léger dépôt
00/06/27	15:35	00/06/30	8:30	17	25.2958	25.3215	24.7524	11.5	(T) Solution jaune pâle, Léger dépôt
00/06/30	18:00	00/07/03	9:40	18	25.2036	25.2315	24.7008	11.8	(U) Solution Claire, Léger dépôt
00/07/03	15:40	00/07/05	8:55	19	25.1678	25.2053	24.6866	12.0	(V) Solution Claire Incolore, Dépôt
00/07/05	14:45	00/07/07	10:45	20	25.1233	25.1427	24.6476	11.2	(W) Solution Jaune Pâle, Dépôt
00/07/10	9:25	00/07/12	9:30	21	25.1425	25.1820	24.6553	11.9	(X) solution jaune, dépôt
00/07/12	14:00	00/07/14	9:35	22	25.1345	25.1616	24.6525	12.1	(Y) solution jaune pâle, léger dépôt
00/07/14	14:48	00/07/17	9:00	23	25.0514	25.0878	24.6123	11.5	(Z) solution jaune
00/07/21	13:00	00/07/24	8:30	24	25.0629	25.1488	24.6300	11.9	(a2) solution jaune, léger dépôt
00/07/24	15:00	00/07/26	0:00	25	24.8878	25.0050	24.5677	12.0	(B2) solution jaune, léger dépôt
00/07/28	13:30	00/07/31	9:30	26	24.8736	24.9997	24.5319	12.2	(C2) solution transparente, léger dépôt
00/07/31	15:30	00/08/02	9:30	27	24.9474	25.1947	24.5831	11.9	(D2) solution transparente, léger dépôt
00/08/04	10:00	00/08/07	9:30	28	25.1167	25.1798	24.5317	11.5	(E2) les solutions ont été jetées
00/08/09	11:30	0/08/14	9:15	29	24.6848	24.8020	24.4211	11.6	(F2) Solution transparente, léger dépôt
00/08/15	9:53	00/08/17	9:50	30	24.4170	24.5525	24.3424	11.6	(G2) Solution jaune claire, dépôt
00/08/17	15:26	00/08/18	9:35	31	24.4512	24.5879	24.3625	11.7	(H2) Solution jaune pâle, léger dépôt
00/08/18	15:00	00/08/21	10:30	32	24.4403	24.5006	24.3524	11.5	(I2) Solution Incolore, Dépôt
00/08/21	15:00	00/08/23	8:15	33	24.5681	24.6933	24.3554	11.9	(J2) Solution incolore, Dépôt
00/08/23	13:30	00/08/25	9:00	34	24.3180	24.5097	24.2985	11.5	(K2) Solution Jaune, Léger Dépôt
00/08/25	15:30	00/08/28	9:06	35	24.1845	24.3376	24.2297	11.8	(L2) Solution jaune pâle, léger dépôt
00/08/29	9:00	00/08/30	9:00	36	24.1319	24.3021	24.2400	11.7	(M2) Solution jaune pâle, léger dépôt
00/08/30	15:20	00/09/01	8:50	37	24.1004	24.2798	24.2175	11.5	(N2) Solution jaune pâle, léger dépôt
00/09/01	15:45	00/09/05	6:54	38	24.0736	24.2627	24.2092	11.6	(O2) Solution incolore, léger dépôt
00/09/05	11:30	00/09/07	9:40	39	24.0479	24.2021	24.1848	11.7	P2 Solution Jaune pâle. Léger Dépôt
00/09/07	14:45	00/09/08	9:00	40	24.0914	24.1976	24.1764	11.4	Q2 Solution Jaune, Léger Dépôt
00/09/08	15:48	00/09/11	8:45	41	24.2863	24.6221	24.2157		R2 Solution Jaune pâle, Léger Dépôt
				42	22.9157	23.0629	23.2727		pour pesées à poids constant #1
				43	22.9049	23.0515	23.2629		pour pesées à poids constant #2
				44	22.9093	23.0554	23.2633		pour pesées à poids constant #3

Interpretation of Data (29 cycles)

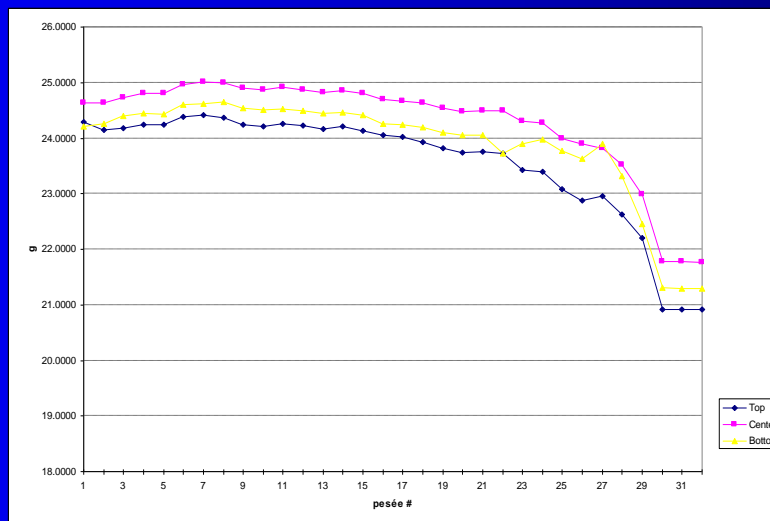
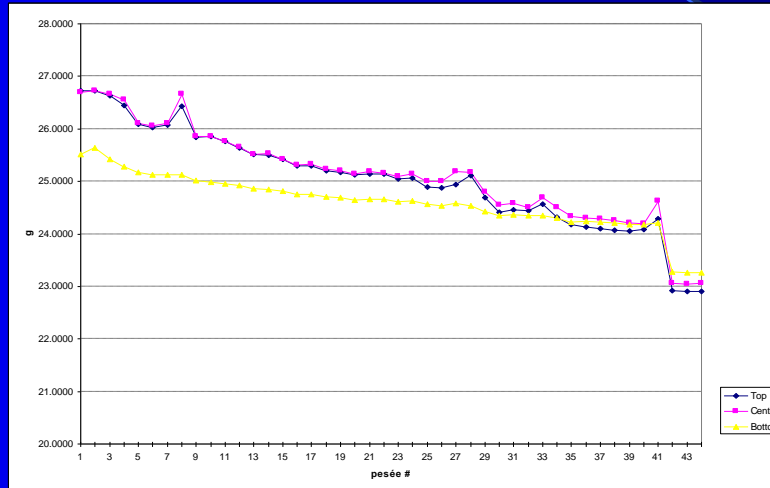


Immersion Testing PU-Polyester Sample "SQ"

Date Entered	Time	Date Out	Time	Cycle	Top	Center	Bottom	ClO2 g/L	REMARKS
00/05/18	15:55	00/05/19	13:00	1	24.2889	24.6405	24.2171	11.9	sln jaune, léger dépôt, mat en surface
00/05/19	16:00	00/05/22	9:30	2	24.1475	24.6330	24.2658	11.8	sln claire, paroi se désintègre
00/05/22	15:40	00/05/24	11:30	3	24.1819	24.7322	24.3935	11.7	sln jaune pâle, léger dépôt
00/05/24	14:30	00/05/26	8:00	4	24.2437	24.8090	24.4470	11.5	sln jaune pâle, léger dépôt
00/05/26	12:25	00/05/29	10:45	5	24.2435	24.8134	24.4361	11.9	sln claire, léger dépôt, paroi se désintègre (top)
00/05/29	16:00	00/05/31	11:50	6	24.3782	24.9673	24.6002	11.3	sln claire, léger dépôt
00/05/31	15:42	00/06/02	11:41	7	24.4223	25.0135	24.6238	12.0	sln claire, dépôt
00/06/02	15:37	00/06/05	7:30	8	24.3731	25.0035	24.6488	12.0	sln claire, dépôt
00/06/07	9:00	00/06/09	9:02	9	24.2450	24.8975	24.5359	11.6	sln claire, dépôt
00/06/09	13:00	00/06/12	10:40	10	24.2150	24.8708	24.5051	12.1	sln claire, dépôt, désintégration des paroi, paroi gonflé (bas)
00/06/12	15:03	00/06/14	9:48	11	24.2597	24.9152	24.5179	11.9	solution jaune pâle, dépôt
00/06/14	15:26	00/06/16	9:17	12	24.2227	24.8760	24.4952	11.9	solution jaune pâle, dépôt
00/06/16	15:50	00/06/19	8:40	13	24.1713	24.8297	24.4458	11.2	solution incolore, léger dépôt, bulle d'air (poche) sur mortier du bas
00/06/19	15:15	00/06/21	9:10	14	24.2077	24.8587	24.4690	11.6	sln jaune pâle, léger dépôt
00/06/21	15:54	00/06/24	10:55	15	24.1366	24.8139	24.4119	12.3	sln claire, dépôt
00/06/24	18:00	00/06/26	9:40	16	24.0532	24.6992	24.2544	12.1	Solution Jaune, Dépôt
00/06/27	15:35	00/06/30	8:30	17	24.0208	24.6730	24.2374	11.5	Solution jaune pâle, Léger Dépôt
00/06/30	18:00	00/07/03	9:40	18	23.9334	24.6300	24.1923	11.8	Solution Claire, Dépôt
00/07/03	15:40	00/07/05	8:55	19	23.8270	24.5480	24.0950	12.0	Solution Jaune, Dépôt
00/07/05	14:45	00/07/07	10:45	20	23.7375	24.4829	24.0526	11.2	Solution Jaune Pâle, Dépôt
00/07/10	9:25	00/07/12	9:30	21	23.7496	24.4963	24.0609	11.9	Solution Claire, Dépôt
00/07/12	14:00	00/07/14	9:35	22	23.7180	24.4910	23.7205	12.1	Solution Claire, Dépôt
00/07/14	14:48	00/07/17	9:00	23	23.4311	24.3054	23.9003	11.5	(Z) solution incolore, léger dépôt
00/07/21	13:00	00/07/24	8:30	24	23.3983	24.2700	23.9709	11.9	(A2) solution incolore , Dépôt
00/07/24	15:00	00/07/26	0:00	25	23.0896	23.9949	23.7707	12.0	(B2) solution jaune, Dépôt
00/07/28	13:30	00/07/31	9:30	26	22.8794	23.8968	23.6386	12.2	(C2) solution transparent, Dépôt
00/07/31	15:30	00/08/02	9:30	27	22.9623	23.8175	23.8913	11.9	(D2) solution transparent, Dépôt
00/08/04	10:00	00/08/07	9:30	28	22.6238	23.5206	23.3100	11.5	
00/08/09	11:30	0/08/14	9:15	29	22.2082	22.9880	22.4542		le mortier s'effrite ,solution transparente, dépôt
				30	20.9228	21.7800	21.3048		pour pesées à poids constant #1
				31	20.9172	21.7758	21.2999		pour pesées à poids constant #2
				32	20.9107	21.7703	21.2955		pour pesées à poids constant #3

Vinyl-Esters Vs. Unsaturated Polyester Mortars

41 Cycles Vs 29 ???



Trial 4 Different cure times on site @180° F CLO₂ @ 11.0 g/l changed every 2.5 days and Wt.'s taken each cycle

- Previous investigations did not reflect true field conditions to which mortars are subjected to during scheduled mill outages.
- A new lab procedure was engineered to include the same mortars but mixed and cured on site at the participating mill for 6 hours, 12 hours and 24 hours.
- These mortars samples were then immersed in a strong CLO₂ solution and monitored every 2.5 days for a period of up to 40 days, or approximately 16 cycles.

Trial 4 On site lab testing

- Proper Mix-Ratio's were taken and recorded.

- Components were then mixed.



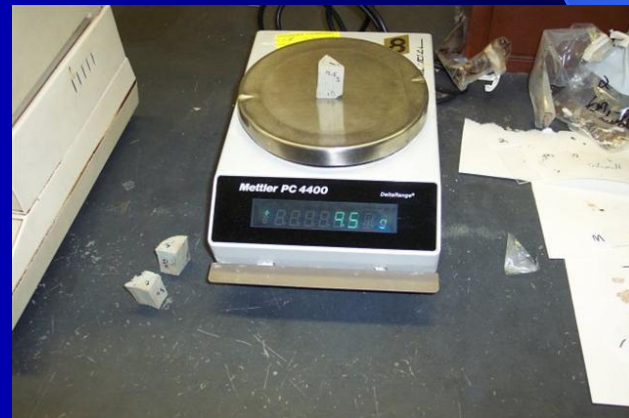
Trial 4 On site lab testing

- Mortar was mixed to a working consistency.
- 1" O.D x 1" H cylinders were formed.



Trial 4 On site lab testing

- Exotherm temperatures were monitored.
- The mass of samples were taken.



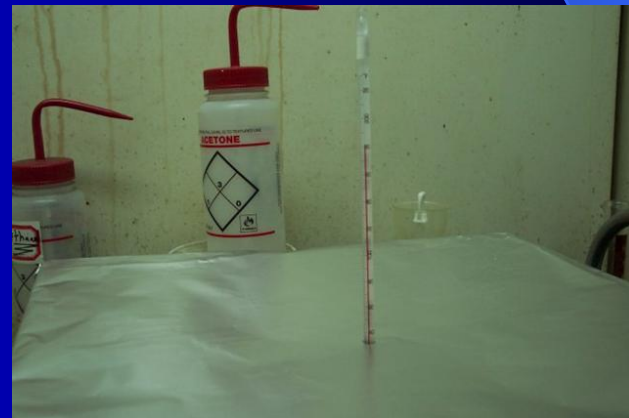
Trial 4 On site lab testing

- Hot water bath was prepared under a fume hood.
- Concentrated ClO_2 solution was introduced to the samples inside a glass vessel.



Trial 4 On site lab testing

- Glass vessels then immersed into the hot water bath and taken up to 180° F
- Samples held for 60 hrs @ process temperature.



Trial 4 On site lab testing

- After the reaction time, glass vessels were taken out.
- Emptied solution and flush distilled water to remove residue.



Trial 4 On site lab testing

- Samples were placed on a heating rack and put in an oven for 2.5 hours. Removed from the oven and placed in a desiccators for 1 hour, so they can cool down in a 0% humidity atmosphere.
- Mass measurements taken, repeated steps.



Trial 4 On site lab testing

- Samples were then re-fortified with ClO_2 solution and re-immersed in the hot water bath.
- Temperature was maintained at 180 deg F



Objective

- To measure the weight loss as a function of its Initial cure to corrosion resistance of AR mortar in a ClO_2 environment within Kraft Bleaching.

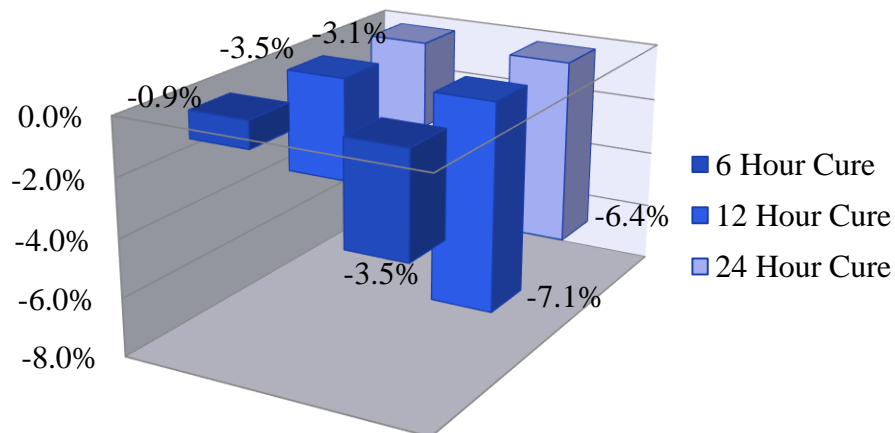


Trial 4 Supplier A Different cure times @180° F ClO₂ @ 11.0 g/l changed every 2.5 days for 40 days

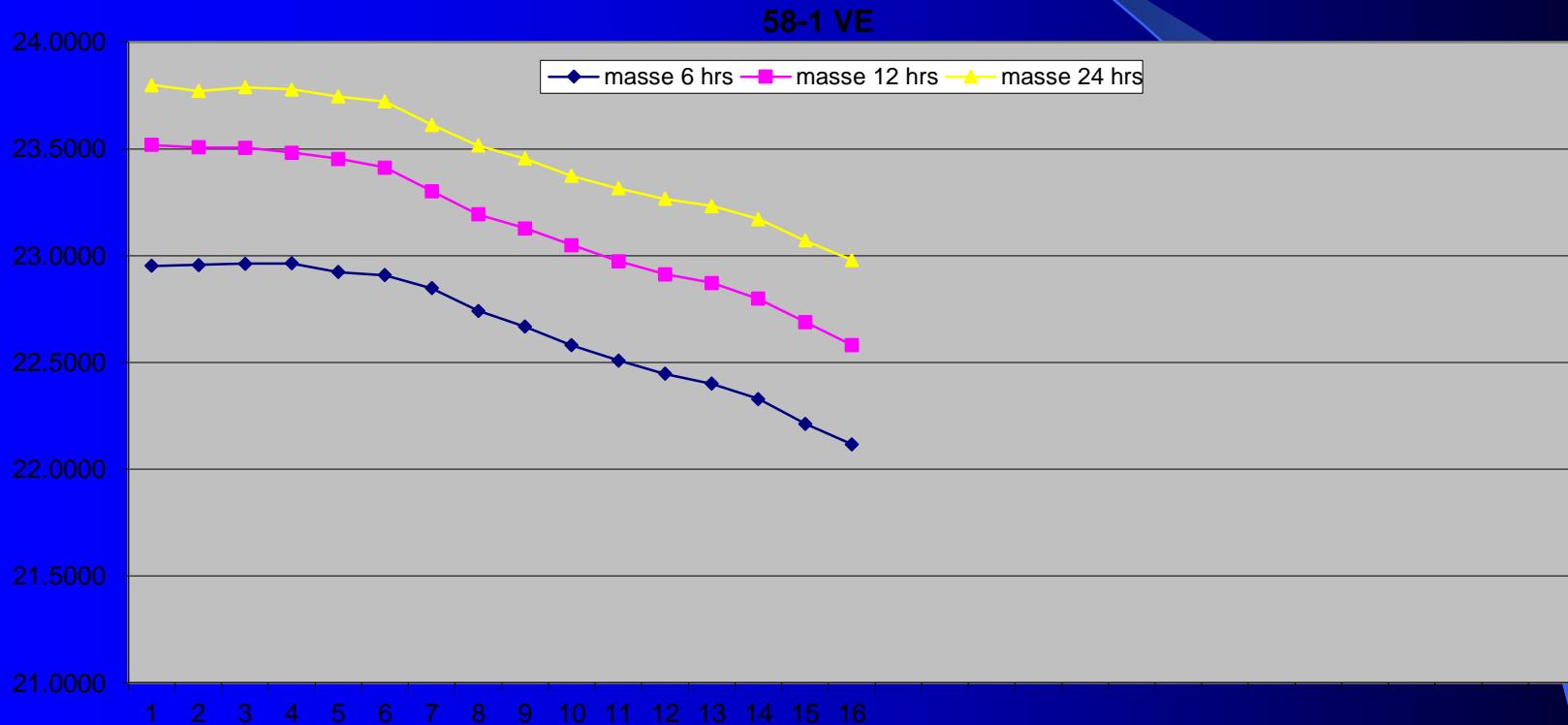
		Exotherm	Mixing T	Set T	Start T 6hr	Start T 12hr	Start T 24hr
A634-58-1 VE	1 liter resin / 2050g powder	58 C	9:50	11:15	16:00	22:00	10:00 + 1 day
A634-58-2 PE - US	1 liter resin / 2425g powder	60 C	10:00	11:30	16:00	22:00	10:00 + 1 day

	A634-58-1 VE		A634-58-2 PE-US	
	Before	After	Before	After
6 Hour Cure	22.9521	22.7418	24.4618	23.6011
Wt. Loss	(8 cycles)	-0.2103	(8 cycles)	-0.8607
% Wt. Loss	(15 cycles 3.2%)	-0.9%		-3.5%
12 Hour Cure	23.5177	22.6886	24.3255	22.594
Wt. Loss		-0.8291		-1.7315
% Wt. Loss		-3.5%		-7.1%
24 Hour Cure	23.7983	23.0717	24.0028	22.4692
Wt. Loss		-0.7266		-1.5336
% Wt. Loss		-3.1%		-6.4%

Trial 4 % Weight Loss T=180°



Trial 4 Supplier A Different cure times @180° F ClO₂ @ 11.0 g/l changed every 2.5 days for 40 days

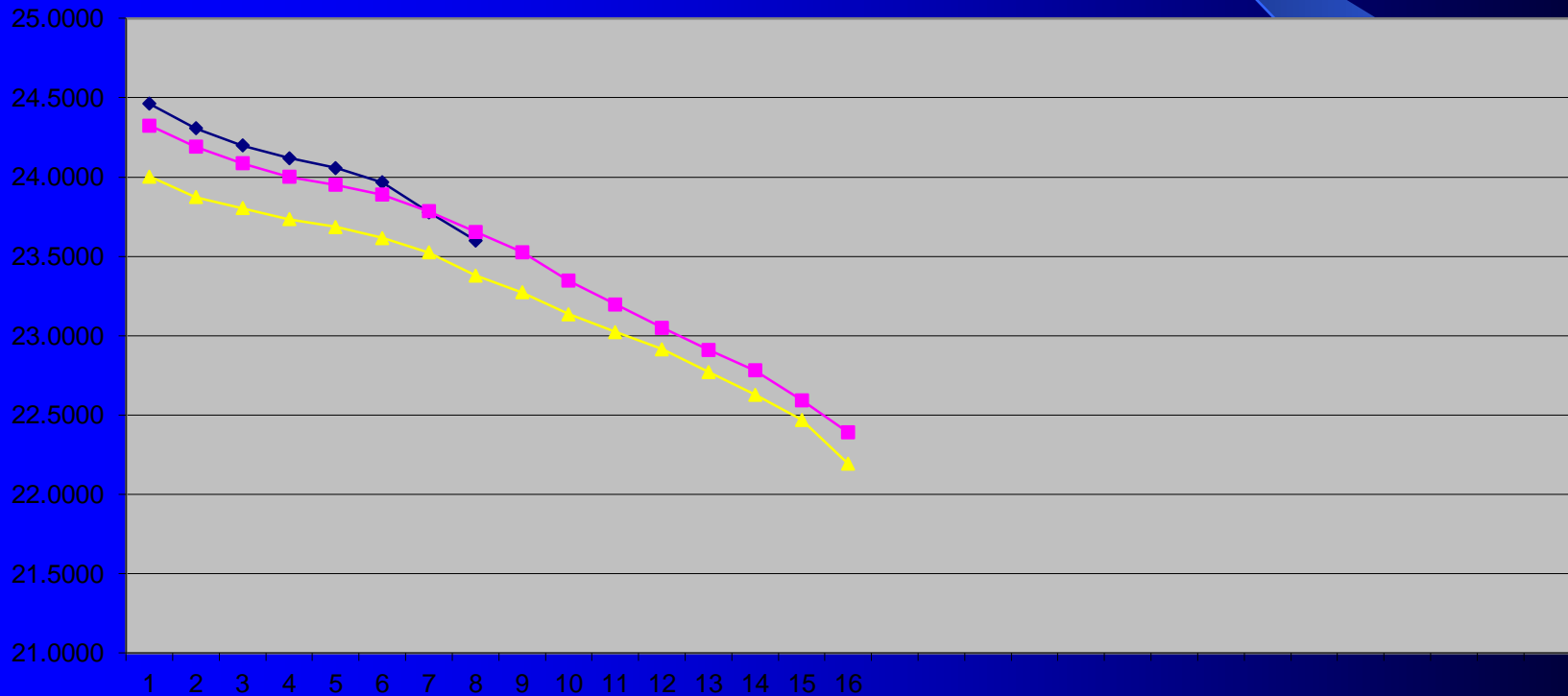


Trial 4 Supplier A Different cure times @180° F ClO₂ @ 11.0 g/l changed every 2.5 days for 40 days

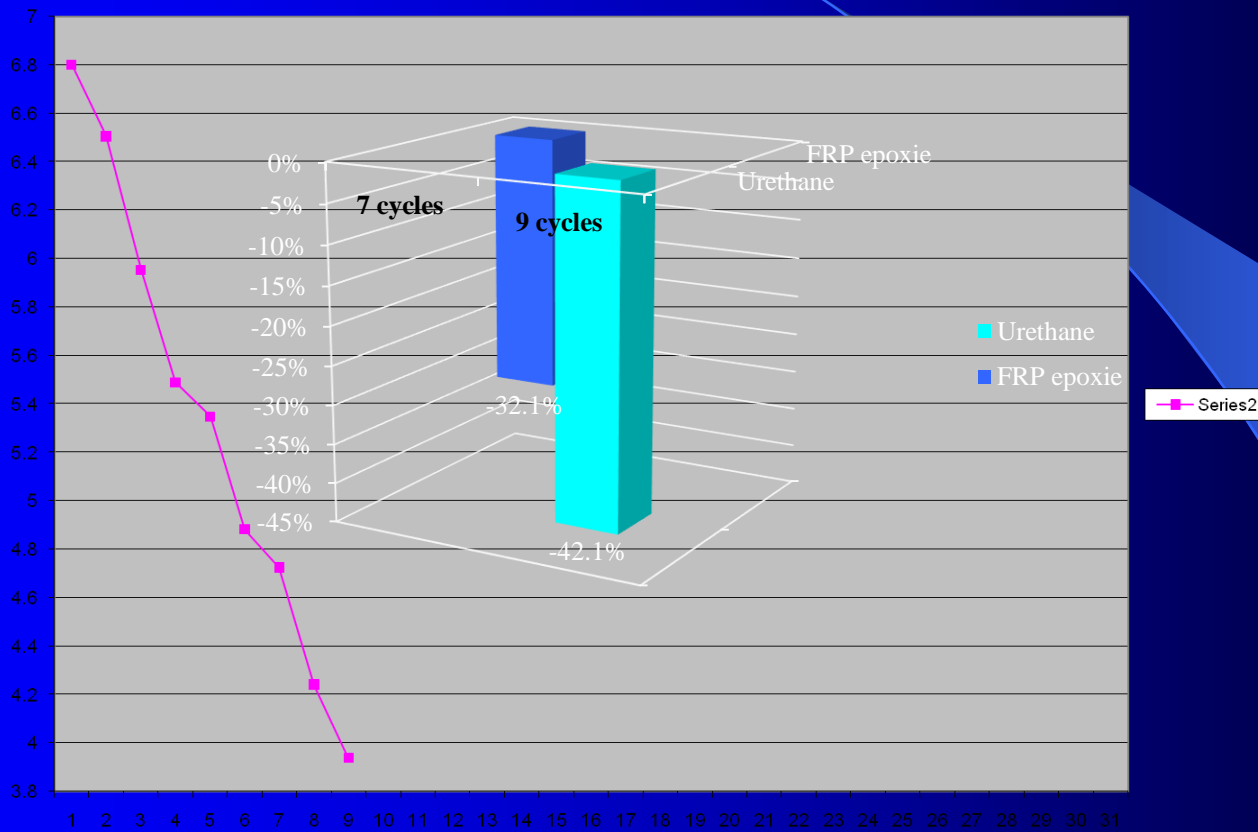
Note 6 hr @ 8 cycles

58-2 PE-US

—◆— masse 6 hrs —■— masse 12 hrs —▲— masse 24 hrs



Trial 4 Testing Urethane Membrane type N & Epoxy FRP laminate in 180° CLO₂ @ 10.8 g/l Cycle = 2 days



Compressive Strength testing

- According to ASTM C 579 the Modulus of Elasticity were measured.

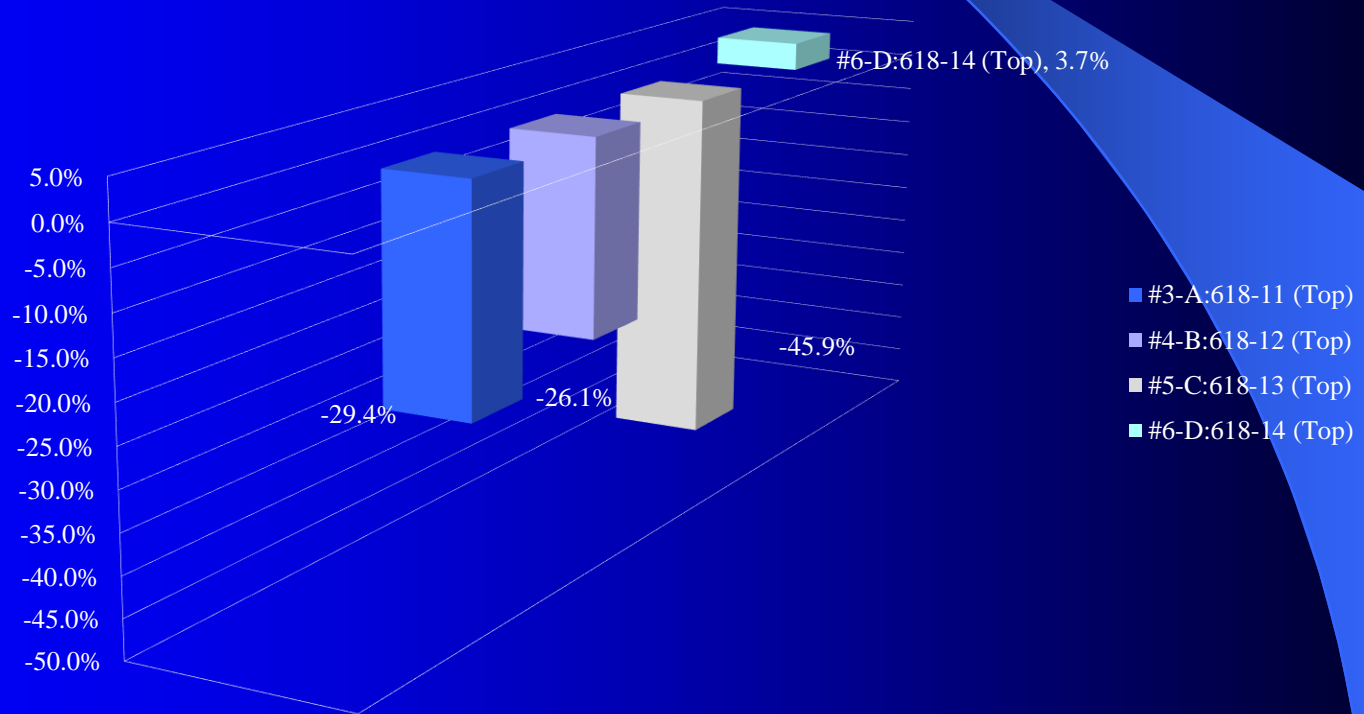


Trial 1 & 3 Supplier A

Trail 3 Compressive Loads After Lab Testing							
	Specimen	Diameter	Area	Machine	PSI	Compressive	Avg.
	Labeled			Reading		Strength +/-	
	#3-A:618-11 (Top)	0.976	0.748	6780	9064	-33.5%	
	(Middle)	0.978	0.751	7400	9854	-27.7%	-29.4%
	(Bottom)	0.978	0.751	7460	9933	-27.1%	
	(Control)	0.999	0.784	10680	13622		
	#4-B:618-12 (Top)	0.987	0.765	7940	10379	-30.3%	
	(Middle)	0.999	0.784	8720	11122	-25.3%	-26.1%
	(Bottom)	0.99	0.770	8860	11506	-22.7%	
	(Control)	1	0.787	11720	14892		
	#5-C:618-13 (Top)	0.977	0.75	5740	7653	-51.6%	
	(Middle)	0.979	0.753	6900	9163	-42.1%	-45.9%
	(Bottom)	0.981	0.756	6700	8862	-44.0%	
	(Control)	0.997	0.781	12360	15826		
	#6-D:618-14 (Top)	0.963	0.728	7760	10659	5.1%	
	(Middle)	0.965	0.731	6940	9494	-6.4%	-3.7%
	(Bottom)	0.965	0.731	6680	9138	-9.9%	
	(Control)	0.991	0.771	7820	10143		
Trial 1	Atlas Mortar -A#73	0.994	0.776	11800	15206	(Avg. of 3 specimens)	
	B#34	1.001	0.787	11200	14231	(Avg. of 3 specimens)	
	C#63	0.993	0.774	12200	15761	(Avg. of 3 specimens)	

Trial 3 Supplier A

Compressive Strength Loss



Trial 4 Supplier D

Compressive Loads: Samples were run to total compressive failure

Before testing the samples were ground flat. After drying at ambient temperature the Compressive Strength according to ASTM C 579 and the Modulus of Elasticity were measured.

1. Results

Sample	Unused / ClO ₂	Compressive Strength		Modulus of Elasticity	
		MPa	psi	MPa	psi
Stellagen G	Control	104	15084	2058	298487
	ClO ₂	46	6672	2121	307625
Stellavol SQ	Control	105	15229	2150	311831
	ClO ₂	32	4641	661	95870

2. Conclusions

Stellagen G mortar: Lost of Compressive strength of 55 % but practically no change in MOE.

Stellavol SQ mortar: Lost of Compressive strength of 70 % but also a lost of MOE (-70).

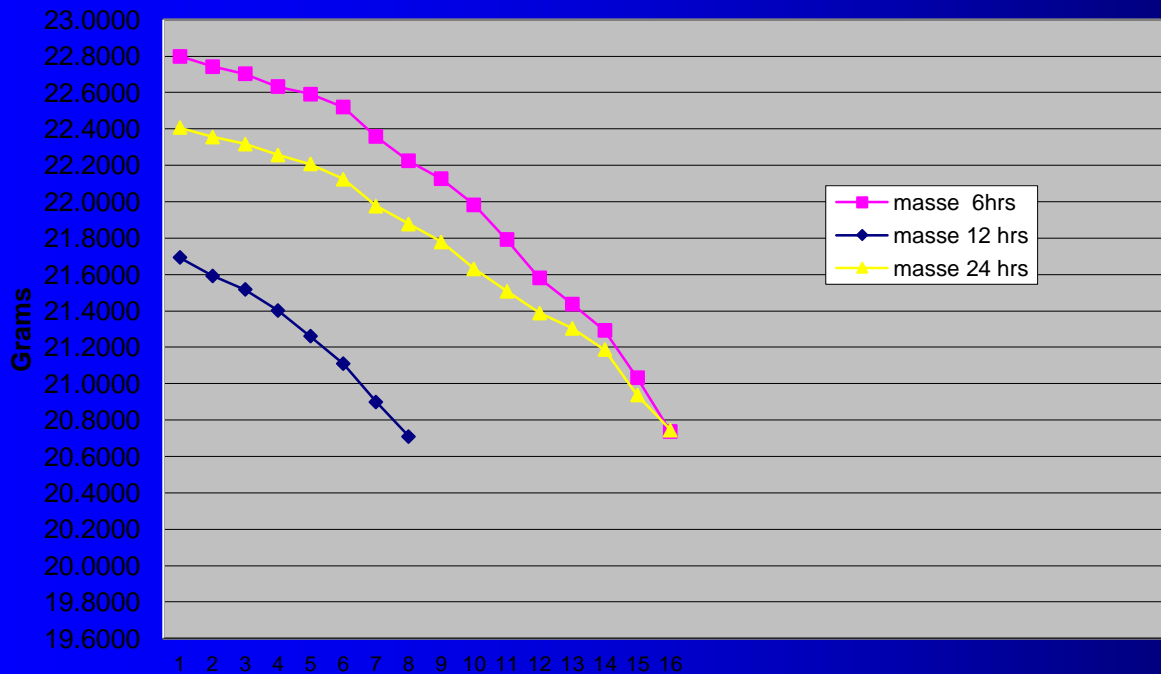
To get a more detailed idea of the corrosion mechanism further investigations with Thermal Analysis and Infrared-Spectroscopy will be needed.

Trial 4 Supplier D

	S solution	Hardner 20	Accelerator A	SQ Powder	Exotherm	Mixing T	Set T	Start T 6hr	Start T 12hr	Start T 24hr
SQ 1 liter resin / 2050g powder	800 ml	65g	20 ml	2200g	53 C	9:20	9:45	15:30	21:30	9:30 + 1 day

	SQ		
	Before	After	
6 Hour Cure	22.79	21.0313	
Wt. Loss		-1.7587	
% Wt. Loss		-7.7%	
12 Hour Cure	21.6932	20.71	only 8 cycles
Wt. Loss		-0.9832	
% Wt. Loss		-4.5%	
24 Hour Cure	22.4082	20.9361	
Wt. Loss		-1.4721	
% Wt. Loss		-6.6%	

SQ



Trial 4 Summary

Study Shutdown Conditions of curing periods of AR mortar

Start = S

Finish = F

Samples / Cycles	Wt. S	Wt. F	Cycles = C	total Wt. Loss	% Wt loss
					S-F/S
SQ = 6 hrs.	22.799	21.0313	15	1.7677	7.8%
SQ = 12 hrs.	21.6932	20.9003	7	0.7929	3.7%
SQ = 24 hrs.	22.4082	20.9361	15	1.4721	6.6%
58-2 = 6hrs.	24.4618	23.7785	7	0.6833	2.8%
58-2 = 12hrs.	24.3255	22.594	15	1.7315	7.1%
58-2 = 24hrs.	23.7983	23.0717	15	0.7266	3.1%
58-1 = 6hrs.	22.9521	22.2132	15	0.7389	3.2%
58-1 = 12hrs.	23.5177	22.6886	15	0.8291	3.5%
58-1 = 24hrs.	23.7983	23.0717	15	0.7266	3.1%
SQ = 28 day (LB)	24.3822	24.4541	15	-0.0719	-0.3%
SQ = 28 day (LB)	24.3822	21.3359	29	3.0463	12.5%
SQ = 28 day (LB)					

Summary

- Approx. 300% difference in compressive strength results from ambient Vs. 180° F
- Any increase in temperatures above 180° F may influence the performance and physical properties of mortars.

Further Testing Completed

- Photo of a DSC (differential scanning calorimetry) Instrument.
- This is used to measure the heat flow into or from a sample under heating, cooling or isothermal conditions.



Summary

Immersion tests of SQ mortar in ClO_2 solutions (10g/l) @ 180° F showed strong attack. Compressive Strength and MOE decreased about 70% and the detected mass loss showed a correlation to the curing time at ambient temperature.

Surprisingly the samples with a curing time of 12 hr were more attacked than the one cured for 6 and 24 hrs.

A kinetic analysis of the resin system should give general information about the curing behavior by calculating a Time-Temperature-Transition-Diagram (TTT-Diagram)

The decomposition of the samples from the immersion test were investigated by thermogravimetric analysis

3. Investigations

3.1 Decomposition

From the cylindrical TAC immersion test cylinders samples were taken from the core and the surface and analyzed by thermogravimetry.

The samples were heated from ambient temperature up to 900°C with a heating rate of 10°C/min. To prevent oxidation reaction a nitrogen atmosphere was used. The decomposition was detected by measuring the mass loss. The results are shown in Fig. 2 + 3:

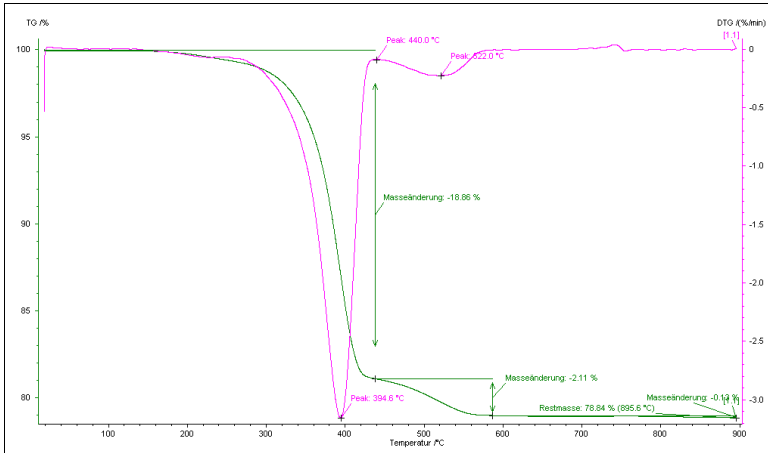


Fig. 2 Thermo gravimetric Analysis: Sample: Stellaval-SQ-Mortar after Immersion Test in ClO₂; unaffected Core

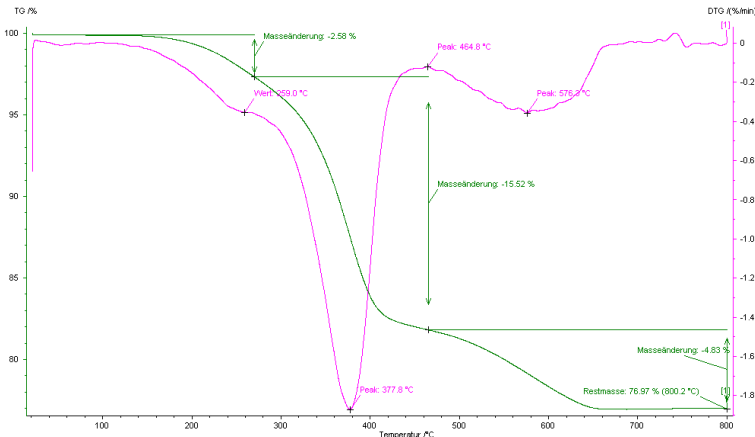


Fig. 3 Thermo gravimetric Analysis: Sample: Stellaval-SQ-Mortar after Immersion Test in ClO₂; Surface

The green curve (TG) shows the mass loss in % and the red one (DTG) is the first deviation (%/min).

The core sample (Fig.2) has two main decompositions at peak temperature 394°C and 522°C. The residue of ignition is 78.8% and is in accordance with our lab samples. The core of the samples was not affected by chlorine dioxide.

The residue of ignition of surface samples (Fig. 3) is in the same magnitude like an unaffected sample, but the decomposition behaviour differs. The first decomposition starts at lower temperature (140°C) with a maximum at 259°C and a mass loss of 2,58% and the second at 377,8°C, -15,52 %. This can be caused by cracking reactions (see 2.1, reaction 1+2).

The increased peak temperature of the third decomposition (576°C) may be caused by the formation of heat resistant chlorinated substances according to 2.1, reaction 3.

All samples (curing time 6, 12, 24 hours) showed the same results in thermo gravimetric analysis.

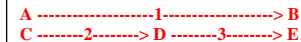
3.2 Kinetic Analysis

For investigation of the curing reaction mixtures of Stellaval S-solution, Hardener 20 and Accelerator A but no fillers were measured with a NETZSCH-DSC-system. DSC (Differential Scanning Calorimeter) is able to detect the heat during the curing reaction of thermosets. For a kinetic analysis it is necessary to measure the curing reaction at different heating rates and with isothermal measurements glass transition temperatures and degree of reaction are detected.

With the NETZSCH-Software "Thermokinetics" the most probably reaction model and reaction type were found.

The Results of the NETZSCH-Software "Thermokinetics" for the most probably reaction model and reaction type are summarized in Fig. 4.

Fig. 4: Reaction Model



Reaction types:

1 : nth order reaction with autocatalysis through the reactant B

$$dA/dt = -A \cdot \exp(-E/RT) \cdot A^n \cdot (1 + K_{cat} \cdot B)$$

log A1 = 2,5181 [1/s]
 E1 = 40,5876 [kJ/mol]
 n = 0,7745
 IndReact. 1 = 0,1930
 log Kcat 1 = 0,8711

2 : nth order Prout-Tompkins reaction with autocatalysis through the reactant D

$$dC/dt = -A \cdot \exp(-E/RT) \cdot C^n \cdot D_a$$

log A2 = 6,5513 [1/s]
 E2 = 57,7874 [kJ/mol]
 n = 1,3345
 a = 0,2760
 FollReact. 2 = 0,7964

3 : n-dimensional nucleation growth according to Avrami / Erofeev

$$dD/dt = -A \cdot \exp(-E/RT) \cdot n \cdot D^{n-1} \cdot (-\ln(1-E))^{(n-1)/n}$$

log A3 = 30,1396 [1/s]
 E1 = 242,7673 [kJ/mol]
 n = 0,5759

The curing reaction is a branched reaction. The first reaction (A→ B) has only a small part (19,3%) of the total reaction.

The main path is the reaction (C→D) and the following reaction (D→ E) with 79 %.

The calculation of the TTT-Diagram using this reaction model is shown in Fig. 5:

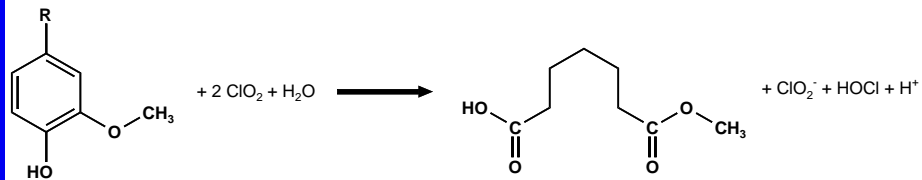
Kinetic Analysis

2. General

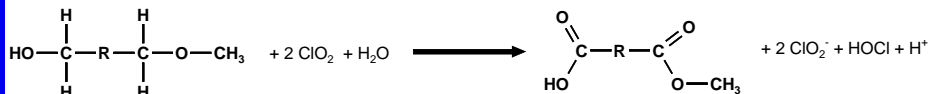
2.1 Known Reactions of Organics with Chlorine Dioxide

Organics are attacked at their functional groups like alcohol, ether and double bonds:

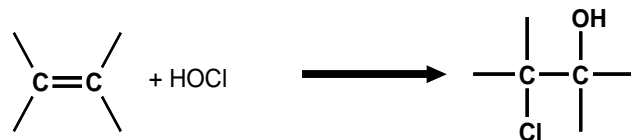
Reaction with aromatic alcohols and ethers



Reaction with aliphatic alcohols and ethers

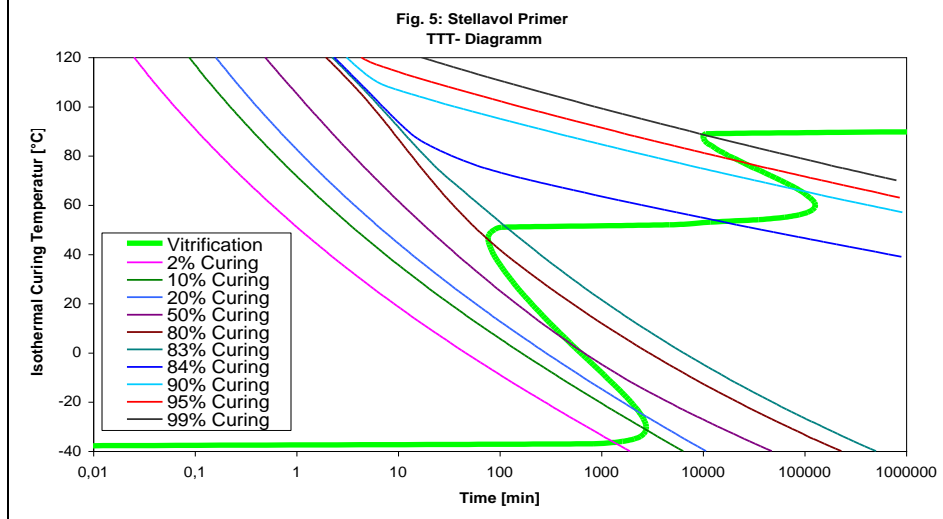


Unsaturated Hydrocarbons with Hypochlorous Acid



2.2 Curing of Unsaturated Polyester

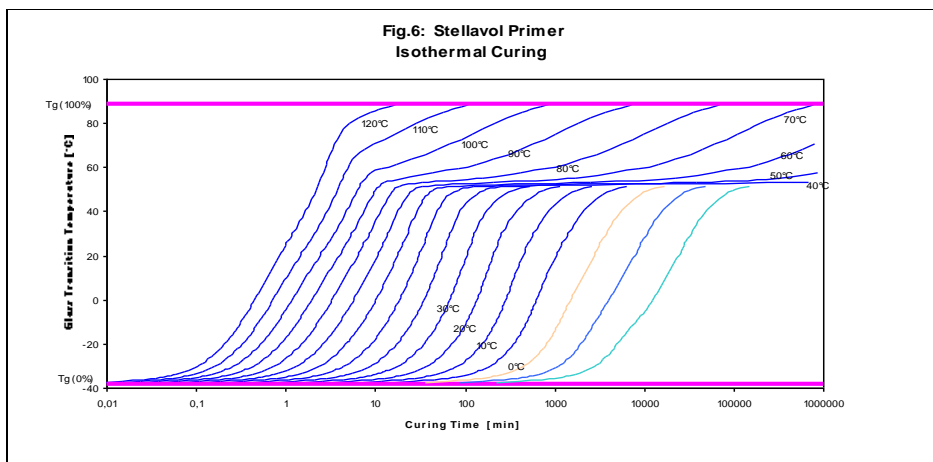
Stellavol S-solution is a polyester dissolved in styrene. The curing occurs via radical polymerisation accelerated by a catalyst (Stella Hardener 20 and Stella Accelerator A).



The TTT-Diagram gives information about the curing rate after isothermal curing dependant on curing time. The thick green line indicates the vitrification border. Left from this border the resin system is liquid or less jellified. The reaction molecules are able to move quickly and the reaction rate is high. Right the green line the system is vitrified and the reaction rate is diffusion controlled because the reacting molecules move very slowly.

At curing temperatures beneath 60°C the curing rate stops between 83 and 84%. To get a total curing temperatures above 60°C were necessary.

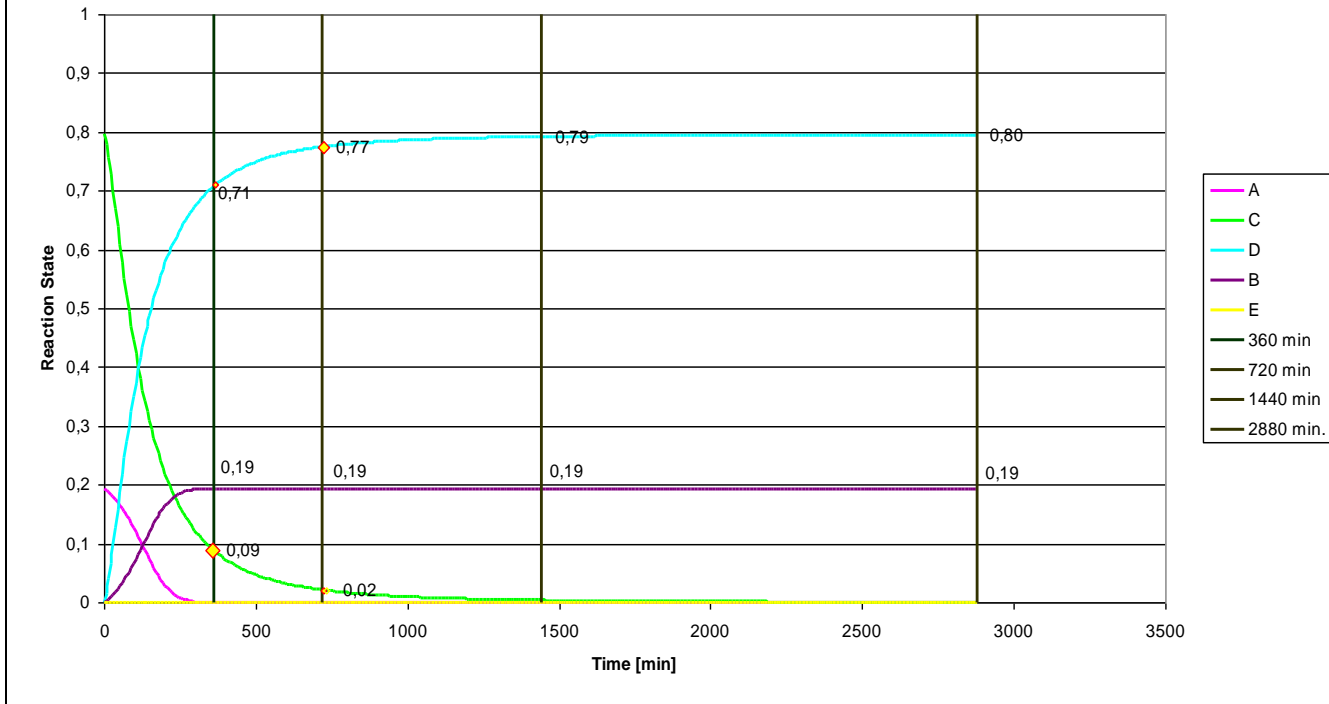
In Fig. 6 shows the dependence of the reached glass transition temperature (= indicator for curing rate) from curing time at several temperatures:



This diagram shows that for total curing within an acceptable curing time temperatures above 90°C are necessary.

Fig. 7 shows the simulation of an isothermal curing at ambient temperature. The state of the curing reaction after 6, 12, 24 and 48 h can be seen:

Simulation of Isothermal Curing of Stellavol-Primer
Curing Temperature: 20°C



After 6 h (360 min) : The reaction (A→B) has finished. 9% of the resin is uncured.
 After 12 h (720 min) : Most of the reaction C→D has finished. 2% of the resin is uncured.
 After 24, 48h : No further reaction. The system is vitrified.

4. Summary

The analysis of the curing reaction gives no explanation for the effect that a curing time of 12 h is worse than 6 and 24 h. After 6 h curing at ambient temperature the curing is practically finished. To get a total curing a temperature above 80°C is necessary.

Conclusions

- Adhesion properties of polyester resin is much greater than vinyl-ester mortars, thereby further promoting curing in damp shutdown conditions. The mortar itself exhibits a pre-wetting feature that is similar to most primers and sealers. Recently a high-bond version in vinyl-ester with thixotropic properties has become available through efforts in working with one supplier. A trial 5 similar to trial 4 will be done testing 6hr, 12hr, and 24 hr cures using only resin with no fillers.



Statement

- The primary failure mechanism involved with premature failure of AR mortar joints in D-stage bleach towers is **“lack of consistence monitoring and documentation, workmanship with quality control and the inability of the mortar to cure under adverse conditions”**.

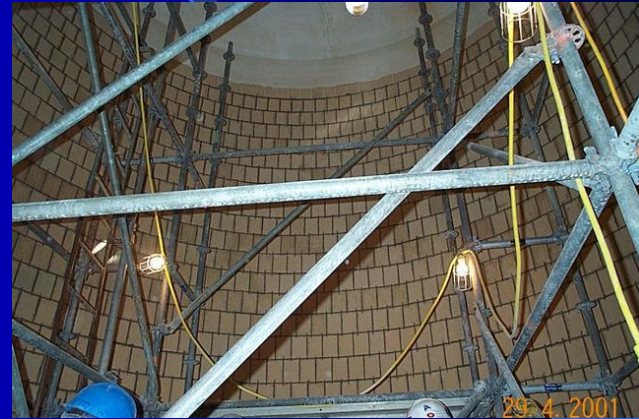
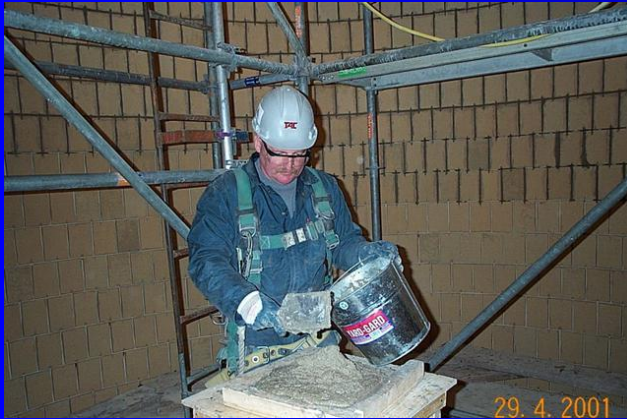
- **Maintaining Joints**



- **Missing Joints**



Typical repointing program



Acknowledgments

John H. Keiser Vice President Atlas Minerals & Chemicals Inc.
Michel Guevremont President Specmont Inc.

Steve Blome President Blome International
Victor Flack Project Engineer Blome International

Horst Feldheiser Special Project Manager Didier Saurebau
Thomas Lichtenberg Chemical Engineer Didier Saurebau

Clarence Koenig Technical Manager St Anne Nackawic
Jacques Parent & Anne Caron Smurfit-Stone

● References

- Characterization of Epoxy Resins Using DSC, Thermal Analysis, W.J. Sichina, National Marketing Manager Perkin Elmer Instruments.
- Thermal Effects of cure Reaction for an Unsaturated Polyester in Cylindrical Moulds, V.Kosar and Z. Gomzi, Dept. of Reaction Engineering and Catalysis, University of Zagreb.
- The Glass Transition Temperature (T_g) As an Index of Chemical Conversion For a High- T_g Amine/Epoxy System: Chemical and Diffusion Controlled Reaction Kinetics G. Wisanrakkit and J.K. Gillham Princeton University