

# Methods for Minimizing or Eliminating Wastewater from Flux Slurries in Non-Corrosive Flux Brazing

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## ABSTRACT

In aluminum heat exchanger production, a non-corrosive flux is applied to individual parts or to assembled units most commonly as an aqueous flux suspension by flooding, spraying or dipping. Wastewater from cleaning the fluxing apparatus and waste flux slurries are often simply diluted and discharged to the environment or treated for fluorides. This paper presents a method for eliminating wastewater from such operations by recycling and reusing the wastewater to make up new flux slurries or to top up existing slurries. Results of flux slurry filtration tests will also be presented. Other alternatives such as a master/process slurry tank configuration are discussed for minimizing the quantity of wastewater.

## INTRODUCTION

In the Nocolok<sup>®</sup> flux brazing process, a potassium fluoroaluminate powder of the general formula  $K_{1-3}AlF_{4-6}$  is used as the fluxing agent. During brazing the flux melts and dissolves the surface oxides of aluminum and prevents further oxidation. The molten flux wets the faying surfaces and allows the filler to flow freely into the joints by capillary action. Upon cooling, the flux remains on the surface as a thin tightly adherent film.

Typically the flux is applied to individual parts or assembled components as a water-based suspension by flooding, dipping or spraying. A surfactant is sometimes added to the flux slurry to aid in wetting and provide uniformity of flux deposition. The suspension concentration, usually in the range of 5% to 25% (w/w) regulates flux loading.

In its simplest form, a flux suspension held in a reservoir tank is continuously agitated to prevent settling. The slurry is pumped, usually with air-diaphragm pumps to the flux spray cabinet where the heat exchangers moving on a conveyor are sprayed with the slurry. After

spraying, the excess flux slurry is blown off in a separate chamber with high volume air. The over-spray and blown-off slurry is recycled back into the reservoir tanks. The volume of flux suspension in the main tank is consumed and therefore must be periodically replenished with fresh flux and water. The amount of flux and water are added in specific proportions to keep the concentration of the flux suspension constant.

With continuous use, a flux suspension will eventually become contaminated with airborne dust, refractory dust, metal fines etc. To date, the authors are not aware of any data or method correlating the level of accumulated contaminants with poor brazing. It is therefore accepted practice that a flux suspension is dumped when there is visual evidence of contamination and replaced with fresh slurry. Discoloration of the suspension is used as the main indicator of contamination. To avoid misjudging the quality of the suspension visually, it is also common practice in some heat exchanger manufacturing facilities to dump the flux suspension at routine intervals. It is also recognized that as heat exchanger cores travel on a conveyor through the flux spray cabinet, splashing occurs resulting in an accumulation of dried flux on the walls of the cabinet. It is also common practice to wash down the cabinet walls to remove the accumulated flux.

In the past, spent flux slurries and water from cleaning the fluxing station or any other water source that came in contact with flux was in many cases diluted and discharged to the environment. In light of heightened environmental awareness and increasingly more stringent wastewater discharge regulations, the practice of discharging to the environment is becoming less and less favorable due to the high fluoride concentration in the wastewater.

All non-corrosive fluxes have a slight solubility in water (up to 4.5 g/l). The purpose of the paper is to show that as an alternative to conventional wastewater treatment practices for fluoride rich wastewater, there are other

options to consider including a complete recycle/reuse method for achieving zero discharge.

## DESCRIPTION OF ZERO DISCHARGE METHOD

Referring to Figure 1, a heat exchanger that has previously gone through a degreasing/de-oiling operation first enters the spray cabinet and is sprayed with an aqueous flux suspension. The excess flux slurry from the over-spray and from the blow-off is re-circulated back to the main slurry tank. When the flux suspension is deemed contaminated (visual determination or after a pre-set time interval) or at such time when the spray cabinet is washed down, the flux-laden wastewater is pumped to a continuously agitated wastewater holding tank. From there, the spent slurry is passed through a filtering arrangement whereby the solids are separated and the particulate-free filtrate is pumped to a filtered water tank. The total volume of the filtered water is adjusted or topped-up with fresh, preferably de-ionized or reverse osmosis water to a level corresponding to the water requirement covering a certain period of time. Adjusting the volume in the filtered water tank with fresh water is necessary because the volume of water to be filtered will always be less than the volume of water consumed for fluxing due to evaporation during the drying stage. If for example fresh flux slurry is needed for each shift, the quantity of regenerated process water should be sufficient to be able to clean the fluxing apparatus, to produce fresh flux slurry and to replace the volume of water consumed during brazing.

When it becomes necessary to replenish the main slurry tank, fresh flux and the regenerated process water from the filtered water tank are utilized. The cycle is repeated indefinitely resulting in zero wastewater discharge<sup>(1)</sup>.

## MASTER/PROCESS SLURRY CONFIGURATION

When considering methods of eliminating wastewater from the fluxing operation, it may not always be possible, for whatever reason to adopt the closed-loop recycle/reuse system described above. In some cases it may be more appropriate to consider ways of drastically minimizing the amount of potential wastewater rather than complete elimination. When this is the case, the master slurry/process slurry tank configuration should be considered.

In the arrangement shown in Figure 2, a large volume of master slurry is prepared and conserved in a tote or tank. The master slurry is kept virtually contaminant free because nothing is recycled back to it. It is simply used to feed the process slurry tank, which is considerably smaller in volume. The volume ratio of master slurry to process slurry is not crucial. The master slurry volume should simply be large enough to feed the process slurry tank for a suitable length of time before being replenished. A 1000 l master slurry and a 50 l process slurry tank (20:1) is an appropriate volume ratio. One

consideration for the size of the process slurry tank is that the total volume of slurry in the entire flux delivery system (volume in plumbing to and from the process slurry tank) is less than the total volume of the tank.

For fluxing heat exchangers, the slurry is consumed from the process slurry tank and the over-spray and excess slurry is re-circulated back to it. As the volume of the slurry in the process slurry tank is depleted, a level indicator would call for top-up from the master slurry. When the process slurry tank does become contaminated either by a visual inspection or by regular dumping, only the volume in that tank must be considered. This greatly minimizes the overall quantity of wastewater generated.

## EXPERIMENTAL METHOD

Several slurry samples including make-up water were collected from various heat exchanger manufacturing sites. The slurry solids were separated from the liquid and the filtrates were analyzed for various potential contaminants. To ensure that brazeability is not compromised when using recycled process water, brazing tests were carried out on the various filtrate samples.

**FILTRATE ANALYSIS** – The slurry samples were filtered using a Büchner funnel vacuum apparatus and No. 40 Whatman filter paper. The weight of the slurry before filtration with the weight of the dried solids after filtration was used to calculate the corresponding slurry concentrations. The pH of each filtrate was measured including the pH of the make-up water for each set of slurry samples. Elemental analysis of the water samples was carried out for the most part by Inductively Coupled Plasma (ICP).

Soluble organic matter in the filtrate samples is expressed by Total Organic Carbon or TOC<sup>(2)</sup>. TOC is a convenient and direct expression of total organic content. Differentiating between various organic species is beyond the scope of this study.

**BRAZING EXPERIMENT** – The angle-on-coupon method was chosen to evaluate the suitability of recycling and reusing water from flux slurries. In this technique, an angle is rested on top of a coupon where the legs of the angle are raised from the surface of the coupon using stainless steel wire. Brazeability is normally measured as a function of the length of the fillet formed after a preset cycle time<sup>(3,4,5)</sup>. In this brazeability study however, certain limitations of the experimental set-up forced the authors to measure the time to form a 100% fillet rather than measuring the length of a fillet after a preset time.

Coupons measuring 25 mm x 25 mm x 0.34 mm were cut from one-sided clad sheet (AA4045/AA3003), then swabbed in acetone to remove residual lubricants. The

angles were prepared from 0.50 mm AA3003 sheet cut in strips measuring 40 mm x 5 mm. The strips were bent in the middle to form a 45° angle in the center.

The coupons were fluxed using a non-corrosive potassium fluoroaluminate flux (Nocolok® flux) by loading the required amount of flux in the center of the coupon corresponding to 6 gm<sup>-1</sup>. A 50 ml aliquot from each filtrate and make-up water sample was set aside for the brazing tests. A drop of Antarox BL225 surfactant was added to each 50 ml aliquot to provide wettability of the water sample on the coupon. Using a micro-pipette, 50 µl of the filtrate was dispensed on the coupon. The filtrate or make-up water was mixed with the flux using a rubber spatula and spread evenly over the surface of the coupon. The coupons were then dried at 80 °C for 1 hour. This technique of flux and water application ensured accurate and reproducible flux and water loadings.

A 23 mm length of 0.23 mm stainless steel wire was laid near one edge of the fluxed coupon, perpendicular to the rolling lines. The angle was placed on top of the wire so that the legs were 1 to 2 mm past the wire. Triplicates were prepared for each filtrate and make-up water sample.

Brazing was carried out in a glass tube furnace under controlled temperature and atmosphere conditions. The angle-on-coupon test specimen was placed on the tray at the entrance of the furnace. The atmosphere was allowed to purge for 1 minute after which the sample was drawn into the heating zone held at 600 °C. The total time for the filler metal to fill the gap up to the stainless steel wire was measured and the average for the triplicate samples recorded.

**FILTRATION TESTS** – An independent laboratory tested a sample of freshly prepared flux slurry for its filterability. The test was conducted by passing a known volume of flux slurry through a filter medium and monitoring the pressure build-up. At a preset pressure, the test was terminated and a number of parameters recorded such as on stream time, filter cake thickness/volume/density and filtrate volume.

## RESULTS

**CASE 1** – This heat exchanger manufacturing site uses a 600 l flux slurry tank for one brazing line. During one work shift, approximately half of the flux slurry is consumed before being topped up. At the end of a work shift, the slurry tank is replenished with flux and make-up water to the original 600 l. A sample of slurry was collected at the beginning of a new shift when the slurry tank is full (ID New Shift Slurry) and at the end of the work shift, but prior to replenishment (ID End Shift Slurry). A sample of make-up water was also collected. The results are shown in Table 1.

**CASE 2** – This brazing line uses a 1300 l slurry tank that is continuously topped up with fresh flux and water. A surfactant is also used for wettability. The analysis of the make-up water and filtrate is shown in Table 2.

TABLE 1. Analysis and Brazing Test Results for Case 1

	Make-up Water	New Shift Slurry	End Shift Slurry
[Slurry]%w/w	N/A	14	14
pH	5.3	5.6	5.5
K (ppm)	<1	543	562
Al (ppm)	<0.1	872	884
F (ppm)	<1	2080	2020
Ca (ppm)	0.15	0.026	0.047
Fe (ppm)	0.11	0.32	0.37
Zn (ppm)	0.02	0.14	0.88
Cl (ppm)	<2	<2	2.1
SO <sub>4</sub> <sup>2-</sup> (ppm)	<3	16	16
NO <sub>3</sub> <sup>-</sup> (ppm)	<0.4	0.80	0.60
PO <sub>4</sub> <sup>3-</sup> (ppm)	<0.09	<0.09	< 0.09
TOC (ppm)	<6	<6	<6
Brazing (sec)	85	116	87

N/A: not applicable

TABLE 2. Analysis and Brazing Test Results for Case 2

	Make-up Water	Slurry
[Slurry]%w/w	N/A	23
pH	5.8	5.0
K (ppm)	17.4	556
Al (ppm)	11.3	1240
F (ppm)	35	2720
Ca (ppm)	0.12	0.048
Fe (ppm)	0.13	0.58
Zn (ppm)	<0.010	0.073
Cl (ppm)	<2	3.4
SO <sub>4</sub> <sup>2-</sup> (ppm)	3.0	20
NO <sub>3</sub> <sup>-</sup> (ppm)	<0.4	0.90
PO <sub>4</sub> <sup>3-</sup> (ppm)	<0.09	<0.09
TOC (ppm)	<6	460
Brazing (sec)	89	90

N/A: not applicable

**CASE 3** – In this brazing line, the components are dipped in the flux slurry. The total slurry volume is about 1585 l with the slurry circulating between the main mixing tank and the dip tank. The volume of slurry in the dip tank is 1140 l while the main mixing tank volume is 445 l. The results of the analysis for the filtrate and make-up water are shown in Table 3.

TABLE 3. Analysis and Brazing Test Results for Case 3

	Make-up Water	Slurry
[Slurry]%w/w	N/A	14
pH	4.9	4.9
K (ppm)	1.11	578
Al (ppm)	0.18	1190
F (ppm)	<1	2760
Ca (ppm)	0.076	0.015
Fe (ppm)	0.10	0.86
Zn (ppm)	<0.010	0.084
Cl (ppm)	<2	32
SO <sub>4</sub> <sup>2-</sup> (ppm)	<3	25
NO <sub>3</sub> <sup>-</sup> (ppm)	<0.4	2
PO <sub>4</sub> <sup>3-</sup> (ppm)	<0.09	<0.8
TOC (ppm)	<6	28
Brazing (sec)	94	105

N/A: not applicable

CASE 4 – The last set of slurry samples were retrieved from a brazing line using a master and process slurry tank configuration (see heading for description). The size of the master tank is about 750 l while the process slurry tank is 40 l for an approximate volume ratio of 18:1 (master slurry:process slurry). The results of the analysis and the brazing tests are shown in Table 4.

TABLE 4. Analysis and Brazing Test Results for Case 4

	Make-up Water	Master Slurry	Process Slurry
[Slurry]%w/w	N/A	4.0	6.3
pH	6.0	5.8	5.7
K (ppm)	13.2	512	510
Al (ppm)	5.88	719	884
F (ppm)	21	1680	2100
Ca (ppm)	0.050	0.045	0.048
Fe (ppm)	0.19	0.31	0.53
Zn (ppm)	0.012	0.061	37
Cl (ppm)	<2	<2	<2
SO <sub>4</sub> <sup>2-</sup> (ppm)	<3	15	20
NO <sub>3</sub> <sup>-</sup> (ppm)	<0.4	<0.4	1.4
PO <sub>4</sub> <sup>3-</sup> (ppm)	<0.09	<0.09	<0.09
TOC (ppm)	<6	<6	7.0
Brazing (sec)	91	89	97

N/A: not applicable

In this case, the slurry sample collected from the process slurry tank looked grayish compared to the milky white appearance of the master slurry sample.

FILTRATION TESTS – Tests were conducted on a laboratory filter press using 2 different pore size polypropylene filter media. The results of the filtration test data are shown in Table 5. P-1 corresponds to a smaller pore size filter media with greater particle retention while P-2 filter media has a larger pore size that would correspond to a higher throughput.

TABLE 5. Results of Filtration Tests

Parameters	P-1 Test1	P-2 Test 2	P-2 Test 3
On stream time (min)	90	60	60
Pressure (bar)	15.5	6.9	6.9
Cake thickness (mm)	25	25	25
Total suspended solids (%)	10.5	10.5	10.5
Weight wet cake (g)	319.6	308.8	351.8
Cake dryness (%)	76.05	74.29	74.98
Volume wet cake (l)	0.164	0.164	0.164
Volume filtrate (l)	2.92	2.01	2.45
Initial volume (l)	3.08	2.17	2.61
Volume reduction (%)	94.7	92.5	93.7

The filtrates in Tests 1-3 were described by the lab conducting the tests as “crystal clear” with only a very slight haze covering the very bottom of the glass container.

## DISCUSSION

ELIMINATING WASTEWATER - This work was initiated as a result of numerous inquiries into treating fluoride rich wastewater from controlled atmosphere brazing lines. More stringent wastewater discharge regulations coupled with environmental awareness programs have forced many heat exchanger manufacturers to consider methods of eliminating or greatly minimizing wastewater discharge to the environment. One method of achieving the goal of complete wastewater elimination is the recycle/reuse method proposed in Figure 1.

The key to successfully achieving zero wastewater discharge from CAB lines is that the regenerated process water must not compromise brazeability. Impurities most likely to contaminate the flux slurry include, but are not limited to plant dust, refractory dust, aluminum fines, corrosion products from fixtures, lubricant, lubricant additives and other non-obvious sources of organic matter. Non-soluble contaminants can be removed by filtration. Soluble contaminants must not interfere with brazing.

In the 4 heat exchanger manufacturing sites where flux slurry samples were obtained, the filtrate analysis showed that K, Al and F were the dominant elements

present with concentrations ranging from 510-563 ppm, 719-1240 ppm and 1680-2760 ppm, respectively.

In all 4 cases, Ca and Fe were present in the filtrate at <1 ppm. Only in Case 4 did the Zn concentration exceed 1 ppm and that is in the process slurry tank of the master/process slurry tank configuration. The 37 ppm Zn in the process slurry filtrate is likely attributed to surface sprayed Zn on condenser tubes. Phosphates were all <0.09 ppm while the highest nitrate concentration was recorded at 1.4 ppm. The sulfate concentration in all 4 cases ranged from 15-20 ppm. The chloride analysis showed Case 3 to have the highest concentration at 32 ppm. The other 3 cases showed the chloride content in the filtrate to range from <2 – 7.2 ppm.

Finally, the TOC of the filtrates of Cases 1, 3 and 4 are <6 ppm – 28 ppm, indicating that very little organic contamination is being tracked into the fluxing station. Case 2 showed a TOC of 460 ppm, but this is accounted for in the fact that a surfactant is added to this flux slurry.

The brazing tests confirmed that brazeability was not compromised when using regenerated process water when compared to flux and fresh make-up water. The 50 µl of filtrate deposited on each coupon was more than adequate to completely wet the surface. Within the parameters of the brazing experiment, the authors believe that any contaminants in the filtrate would affect the performance of the flux and/or the ability of the filler metal to fill the gap and therefore the time to fill the gap. In cases 2, 3 and 4, the difference in brazing time between samples prepared with fresh make-up water (control) and filtrate was 1 second, 11 seconds and 8 seconds, respectively. Case 1 showed one instance where the difference in time was 31 seconds (new shift slurry), but the end shift slurry filtrate showed a difference of only 2 seconds, suggesting that the new shift slurry filtrate brazing test might be anomalous. No matter what the interpretation, the brazing tests showed that there were certainly no gross effects on brazing time when using regenerated process water.

**MINIMIZING WASTEWATER** – If the closed loop wastewater recycle/reuse option is not viable, the master/process slurry tank configuration could be considered. The concentration of impurities in the process slurry tank is only very slightly higher in most cases than in the master slurry tank. Even though the entire volume of excess slurry from the fluxing station is recycled into one small tank, the turnover of fresh flux slurry from the master tank into the process slurry tank is rapid due to high consumption. This keeps the overall chemistry in the process slurry very close to that of the master slurry.

Finally, the grayish appearance of the process slurry sample was likely due to insoluble matter (metal fines, dust and so on) because the chemistry of the master and

process slurry filtrates were so similar. This is further evidence that the filtrate from discolored slurry can be recycled and reused.

**SLURRY FILTRATION** – The results of these tests indicate that the flux slurry is easily filterable. There was a gradual build up of pressure on the filter media as the thickness of the cake increased. No anomalous behavior was observed. The haze covering the very bottom of the filtrate jars is attributed to a few sub-micron flux particles not trapped by the filter media. According to the lab conducting the experiments, this is normal behavior for this type of powder.

## CONCLUSION

Filtrate analyses and brazing tests show that a closed loop system for recycling/reusing fluoride rich wastewater is a viable method to attain the goal of zero wastewater discharge in non-corrosive fluxing brazing operations. Greatly minimizing the volume of wastewater can be achieved by adopting a master/process slurry tank configuration.

By combining the beneficial nature of the master/process slurry tank configuration with the closed loop method of recycling/reusing fluoride rich wastewater, it is possible to obtain zero discharge with minimum waste flux slurry handling.

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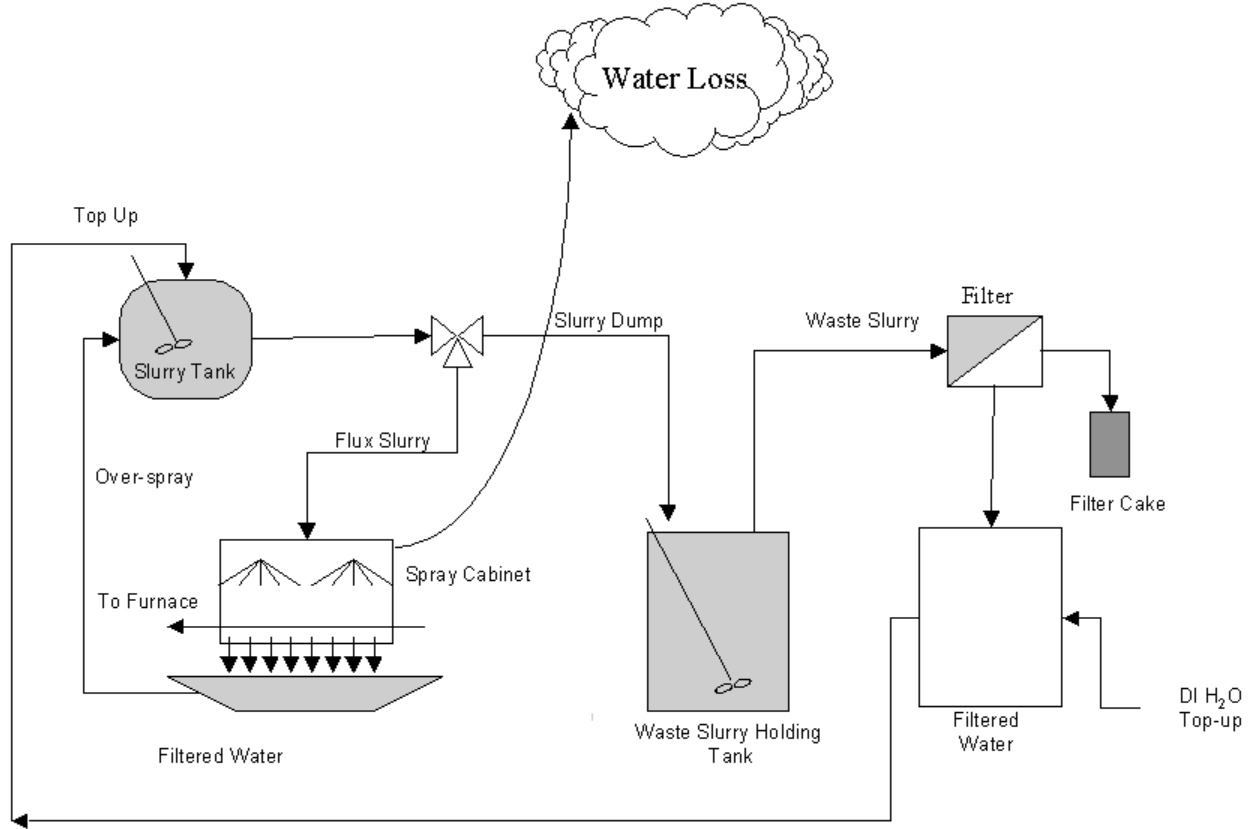
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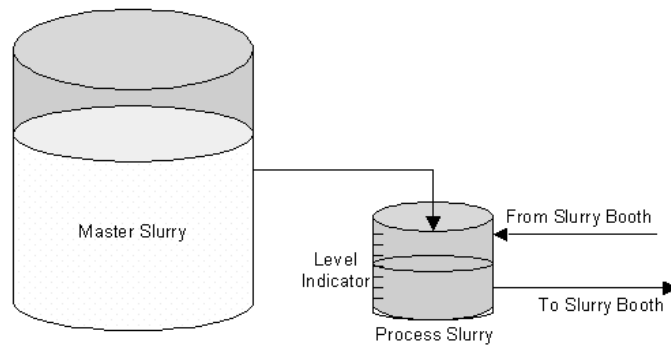
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**Figure 1.** Schematic Showing Arrangement for Closed Loop Wastewater Recycle/Reuse Method



**Figure 2.** Schematic of Master/Process Slurry Tank Configuration