The Myths of NOCOLOK®

Myths about Aluminium Brazing with Non-Corrosive Fluxes

NOCOLOK® Flux Brazing Technology
Myths about Aluminium Brazing with Non-Corrosive Fluxes

NOCOLOK® Flux Brazing Technology

Daniel C. Lauzon
Solvay Fluorides, Inc., St. Louis, MO, USA

Hans-Walter Swidersky
Solvay Fluor und Derivate GmbH, Hanover, Germany
# Table of Contents

**Introduction**  
5

**Myth No. 1:** A Flux with Smaller Particle Size is More “ACTIVE” and Leaves Less Flux Residue  
6

**Myth No. 2:** Fluxes With a Lower Melting Range are Superior  
9

**Myth No. 3:** Some Fluxes Produce Less Hydrogen Fluoride (HF) than Others  
10

**Myth No. 4:** “Pure” Flux Compounds (i.e. “Pure” Fluxes) are Better for Brazing  
13

**Myth No. 5:** Non-Corrosive Fluxes Absorb Moisture (i.e. NOCOLOK® Flux is Hygroscopic)  
15

**Myth No. 6:** More Flux is better  
16

**Myth No. 7:** Flux Slurry Concentration is the Only Factor to Control Flux Load  
17

**References**  
18

**More Information**  
19
or nearly 20 years, NOCOLOK® Flux brazing – or Controlled Atmosphere Brazing (CAB) with non-corrosive fluxes – has been the preferred process for producing aluminium automotive heat exchangers. In the two decades since the process was first introduced to the automotive world, a great deal has been learned about flux handling, flux application, flux performance, and process optimisation. In fact, the sophistication of today’s CAB brazing furnaces, combined with years of process improvements, has reduced typical flux loads by almost 50%.

Despite the fact that CAB brazing is a mature technology, over the years many misconceptions about certain flux properties have been spread and falsely accepted. In many cases these misconceptions have caused confusion with the heat exchanger manufacturers where decisions are made based on circulated fiction rather than actual facts.

The intention of this publication is thus to address the most popular myths and comment on their technical merits based on published literature, fundamental chemistry and Solvay’s own research work. We hope to encourage the reader to deal only with the facts about NOCOLOK® Flux brazing, to promote a better understanding of non-corrosive flux properties and use.
Based on the above information, the authors strongly believe that the amount of hydrogen fluoride generated is not flux-specific, but depends on several factors such as:

- Flux load (i.e., quantity) going through the furnace – flux loading and component throughput
- Temperature profile – heating rate and time at temperature
- Furnace atmosphere conditions such as nitrogen flow and dew point

There is no evidence to suggest that some fluxes produce less HF than others.
A Flux with Smaller Particle Size is More “ACTIVE” and Leaves Less Flux Residue

Some rumours have been spread that a flux with a smaller particle size leads to better brazing and results in a more pleasing post-braze appearance. But the facts are very different.

It is true that a flux with a smaller particle size covers the surfaces of the work-piece more completely than the same quantity of flux with a larger particle size. Smaller flux grains will also adhere better to those surfaces, assuming that the two fluxes to be compared indeed show a difference in particle distribution.

As particle size decreases, the total surface area of the flux increases. This allows a higher surface area of flux to be in contact with the work-piece. During heat up, there may be more efficient energy transfer to the flux with the smaller particle size. The net result is that this would affect the kinetics of melting – how quickly the flux melts – but it does not affect the melting temperature range. This is analogous to crushed ice melting quicker than a block of ice, but both melt at the same temperature. Figure 1 shows the melting action of various particle size fluxes using Differential Scanning Calorimetry or DSC. As expected, all particle sizes melt at precisely the same temperature.

Figure 1: DSC Scans for Granulated NOCOLOK® Flux Samples
Myth No. 1

It is also speculated that the ability of the flux to melt and spread (activity) increases as particle size decreases. In fact, the activity of the flux is related to chemistry and phase composition, not particle size. Spreading is simply a liquid phase reaction unrelated to the particle size distribution of the solid phase.

A practical example showing how flux particle size is unrelated to brazing results is comparing NOCOLOK® Flux (average particle size 2 – 6 µm, see Figure 2) used for wet fluxing with NOCOLOK® Flux Drystatic (average 3.5 – 25 µm, see Figure 3) used for electrostatic fluxing. Heat exchangers brazed by wet fluxing can be brazed with the same results using dry fluxing, and the only difference is the particle size of the flux. The success simply depends on applying the flux uniformly.

Finally, the appearance of the post-braze surface is only related to the initial flux loading, not particle size. Once the flux melts, it is completely liquid. In its molten state, the flux has no particles – neither large nor fine. Once the flux is liquid, it immediately spreads out and wets the surfaces. Upon cooling and solidification, the amount of flux residue and its distribution on the surface of the work-piece is related entirely to the initial flux loading, and not particle size.

It is true that particle size distribution of a flux affects slurry characteristics. A finer powder will stay longer suspended (i.e. it settles slower) than a coarser product. Material with larger grains seems to build-up more rapidly on inside surfaces of slurry tanks and spraying equipment. Regardless of the specific particle distribution of a flux, continuous agitation is necessary to prevent settling and build-up. Regular maintenance is the only way to avoid the formation of solidified material residues.
Myth No. 1

Figure 2: Typical Particle Size Distribution for NOCOLOK® Flux Used For Wet Application

Figure 3: Typical Particle Size Distribution for NOCOLOK® Flux Drystatic Used For Dry (Electrostatic) Application
Fluxes With a Lower Melting Range are Superior

There are claims that a lower melting point flux is better for brazing (i.e., melting between 550 and 560°C – approximately 10–15°C below conventional fluxes). The idea here is to try to fool the engineer by illustrating the merits of “early” flux melting, and thus “prolonged” flux action. However, the facts are very different.

As soon as the flux begins to melt, one of the components of the flux – KAlF₄ – begins progressively evaporating, with a vapour pressure determined to be 0.08 mbar at 600°C(2). Evaporation of KAlF₄ causes the flux melt to change composition, and it begins to dry out. Given enough time, it is possible for the flux melt to completely dry out before reaching the maximum peak brazing temperature.

A good brazing flux only needs to be available just before filler metal melting. Table 1 describes what happens at brazing temperature:

<table>
<thead>
<tr>
<th>Surface Temperature of Aluminium Components</th>
<th>Temp. Range Δ</th>
<th>Action</th>
<th>Duration with a Heating-Ramp of 25°C/min</th>
<th>Duration with a Heating-Ramp of 15°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 560°C</td>
<td></td>
<td>Uniform heat-up</td>
<td></td>
<td>Depends on brazing cycle</td>
</tr>
<tr>
<td>Between 560 and 575°C</td>
<td>15°C</td>
<td>Flux melting</td>
<td>0.6 min = 36 sec</td>
<td>1 min = 60 sec</td>
</tr>
<tr>
<td>Between 575 and 585°C</td>
<td>10°C</td>
<td>Flux spreading and surface wetting</td>
<td>0.4 min = 24 sec</td>
<td>0.66 min = 40 sec</td>
</tr>
<tr>
<td>Approximately 585–605°C</td>
<td>20°C</td>
<td>Brazing range of AA 4045 filler alloy</td>
<td>0.8 min = 48 sec</td>
<td>1.33 min = 80 sec</td>
</tr>
<tr>
<td>Approximately 590–610°C</td>
<td>20°C</td>
<td>Brazing range of AA 4343 filler alloy</td>
<td>0.8 min = 48 sec</td>
<td>1.33 min = 80 sec</td>
</tr>
</tbody>
</table>

As soon as the flux melts, it begins to dissolve the oxide layer, and this solvating process continues until the oxide is removed, even if the filler alloy has melted. The above table shows that even if the period of flux activity would be limited only to the time between complete flux melting and the lower brazing range of AA 4045, it is still adequate. The authors thus consider a flux melting range between 560 and 575°C as the most suitable for aluminium brazing with Al-Si filler alloys.

One should not completely dismiss the point made about “prolonged” fluxing action with lower melting point fluxes. However, once again, all the information must be examined. Yamaguchi et al. have shown that with an increase in the K₂AlF₅ content, the flux will start to melt at a lower temperature so that the flux will work at a lower temperature. However, even if KAlF₄ evaporation is ignored, the same study concluded that increasing the K₂AlF₅ content eventually prevents the flux from spreading smoothly, and therefore affects the efficiency of the flux(1).

The evidence presented here is sufficient to demonstrate that merely lowering the melting point does not in itself create a better brazing flux.
Some Fluxes Produce Less Hydrogen Fluoride (HF) than Others

Although there are several brands of non-corrosive aluminium brazing fluxes, at brazing temperature, they are all understood to be a mixture of KAlF₄ and K₃AlF₆. When heated up to brazing temperature, one of the flux components (KAlF₄) starts to evaporate in small quantities. The fumes produced by evaporating flux contain fluoride, and can potentially react with moisture traces present in the gas phase (from surrounding atmosphere) to form hydrogen fluoride (HF).

This is conclusive for several reasons. The flux has a measurable vapour pressure. Thompson and Goad have measured the vapour pressure of KAlF₄ over the flux melt to be 0.08 mbar at 600 °C(2). Takemoto et al. revealed in their experiments that the mass of a KAlF₄ – K₃AlF₆·H₂O type flux decreased during brazing because of evaporation. At 600°C, they determined that the rate of flux loss was 0.02 µg/sec(3). Solvay’s own TGA analysis (with a heating rate of 20 °C/min, see Figure 4), showed that the quantity of volatile compounds in NOCOLOK® Flux between 250 °C and 550°C is approximately 0.2 to 0.5 wt %.

Figure 4: Differential Thermal Analysis (DTA) Diagram for NOCOLOK® Flux (Batch 4090) – Heating Rate 20°C/Min

long with most other aluminium brazing fluxes on the market, NOCOLOK® Flux is an inorganic fluoride salt consisting of potassium fluoroaluminates of the general formula K₁₋₃AlF₄₋₆. Fluxes of this type are considered intrinsically non-corrosive in that they are non-hygroscopic, they do not react with aluminium whether solid or molten, and can remain on the surfaces of brazed components as a thin, tightly adherent and inert residue.
It is clear that all fluxes will create flux fumes, with strong evidence suggesting that the vapour primarily contains KAlF₄. With regard to CAB brazing (furnace brazing) where traces of moisture are always present even at -40 °C dew point (which corresponds to 106 ppm H₂O at atmosphere pressure), a number of compounds can be formed in the system K – Al – F – H – O. To our knowledge there has been no academic effort to create a thermodynamic model of this system. Thus, it is impossible to predict which compounds will and will not exist, and in what temperature or humidity regimes. This is why more than one mechanism has been proposed for the generation of HF, but no unique reaction mechanism has been identified:

\[
\begin{align*}
3 \text{KAlF}_4 + 3 \text{H}_2\text{O} & \rightarrow \text{K}_3\text{AlF}_6 + \text{Al}_2\text{O}_3 + 6 \text{HF} \\
2 \text{KAlF}_4 + 3 \text{H}_2\text{O} & \rightarrow 2 \text{KF} + \text{Al}_2\text{O}_3 + 6 \text{HF}
\end{align*}
\]

While the evidence above points to gas phase reactions between flux fumes and water vapour for the generation of HF, Thompson and Goad (2) also proposed that AlF₃ dissolved in the flux melt is subject to hydrolysis according to:

\[
2 \text{AlF}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6 \text{HF}
\]

What is clear is that in all cases, HF is shown as a reaction product. As for the quantity, Field and Steward have indicated that the amount of HF formed is typically 20 ppm in the exhaust of a continuous tunnel furnace (4). Solvay’s research work confirmed that even when flux on aluminium is heated in a bone-dry nitrogen atmosphere, a small quantity of HF is still generated (5). A source of hydrogen must be made available for HF to be formed even under bone-dry conditions, and this might include reduction of aluminium hydroxide, degassing of furnace walls, leakage or other less obvious sources. The work proved that even under ideal conditions, it is virtually impossible to avoid some trace HF formation.

![Diagram 1: HF Generated as Function of Moisture Content](image.png)
ome believe that pure flux phases such as pure KAlF$_4$ or K$_2$AlF$_5$ are better for brazing than mixtures of phases. Some have even referred to the presence of K$_2$AlF$_5$ as an “impurity”. This could not be further from the truth.

The efficiency of a flux is characterised by a combination of factors such as melting and spreading, fillet formation and clearance filling. Yamaguchi et al. showed that the pure flux phases, namely KAlF$_4$ and K$_2$AlF$_5$, are not the most efficient in optimising these flux characteristics$^{(1)}$. In fact, they showed the flux to be highly effective when a combination of KAlF$_4$ and K$_2$AlF$_5$ was used. Furthermore, the presence of K$_2$AlF$_5$ is necessary to achieve the proper ratio of KAlF$_4$ and K$_3$AlF$_6$ at brazing temperature, the necessary condition to form the eutectic. This can be explained more thoroughly by examining the following schematic:

<table>
<thead>
<tr>
<th>Flux Components – Phase Transformation During Brazing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>As Manufactured</strong></td>
</tr>
<tr>
<td>KAlF$_4$ and K$_2$AlF$_5$ · H$_2$O</td>
</tr>
<tr>
<td>90°C–150°C</td>
</tr>
<tr>
<td>90°C–150°C</td>
</tr>
<tr>
<td>K$_2$AlF$_5$ (I)</td>
</tr>
<tr>
<td>290°C–330°C</td>
</tr>
<tr>
<td>K$_2$AlF$_5$ (I)</td>
</tr>
<tr>
<td>and/or K$_2$AlF$_5$ (I) + (II)</td>
</tr>
</tbody>
</table>
As manufactured, a flux typically contains a mixture of KAlF₄ and K₂AlF₅, where the K₂AlF₅ may or may not be hydrated (see Figure 5: “Typical XRD Diagram of NOCOLOK® Flux”). During the brazing process, the material undergoes essential physicochemical transformations. While the chief component, KAlF₄, is simply heated up, the compound K₂AlF₅ · H₂O begins to lose its crystal water from 90°C on. When the temperature is further increased within the ranges of 90°–150°C, and 290°–330°C, two different crystallographic modifications of K₂AlF₅ are formed. When the furnace temperature is raised above 490°C, K₂AlF₅ begins to dissociate:

\[
2 \text{K}_2\text{AlF}_5 \rightarrow \text{KAlF}_4 + \text{K}_3\text{AlF}_6
\]

The exact amount of K₂AlF₅ necessary for a eutectic flux composition is obtained from the original K₂AlF₅ content. It is the ratio between the total amount of KAlF₄ (as manufactured and dissociation of K₂AlF₅) and K₃AlF₆ that forms the basis for flux melting.

In fact, the flux manufacturer chooses the ratio of KAlF₄ and K₃AlF₆ based on the eutectic AlF₃-KF phase diagram (see left), which was first constructed in 1932 and further researched and refined in 1966.

There can be no doubt that a flux must contain more than just the pure phases – and it must contain these phases in an extremely precise ratio – in order to work effectively and to meet the conditions for eutectic formation which controls the melting point.
Myth No. 5

Non-Corrosive Fluxes Absorb Moisture (i.e. NOCOLOK® Flux is Hygroscopic)

Hygroscopicity should not be mistaken for the simple physical adsorption of humidity on a powder surface. Moisture generally adheres to all surfaces depending on the humidity level of the surrounding atmosphere, the surface structure and surface area, as well as temperature and pressure conditions. Physical adsorption involves neither a chemical reaction nor any dilution or liquefying. Adsorption on powder surfaces may result in agglomerations or clumping, however, these effects are reversible. When the humidity level of the surrounding air decreases or the powder surface temperature increases, the adsorbed water molecules are released (desorption) until a balance of the system is again reached.

On a more practical note, the authors have tried to analyse the difference in moisture content of some powder samples used in electrostatic fluxing. One sample was taken from a fluxing booth to which moist air had access. Poor fluidisation of the flux powder was observed, resulting in agglomerates. The other sample was from a fluxing booth in which dried air was used and no performance problems were reported. Both samples were shipped to our lab for analysis. The results demonstrated only the loss-on-heating (LOH) related figures (see next paragraph), and no difference was found between the two samples. What happened was simply that the material, which had adsorbed some humidity in the fluxing booth, had lost all of this adsorbed moisture before it could be analysed.

NOCOLOK® Flux does not chemically react with moisture, and thus is not hygroscopic!
Myth No. 6

More Flux is Better

An initial flux load that is too high will result in excess post-braze flux residue. Flux drips (i.e. visible crystalline residue) can form on the product and downgrade appearance. In some cases, excess flux residue can cause problems with gaskets and seals, as well as with surface treatments after brazing (e.g. painting).

Over-fluxing can lead to more rapid flux build-up on the fixtures and increase the maintenance intervals.

Over-fluxing is a waste of flux, which will inevitably increase process costs.

While “more flux is better” is true in some circumstances, there is an overwhelmingly negative impact from increasing the flux load to compensate for some process deficiencies.

An initial flux load that is too high will result in excess post-braze flux residue. Flux drips (i.e. visible crystalline residue) can form on the product and downgrade appearance. In some cases, excess flux residue can cause problems with gaskets and seals, as well as with surface treatments after brazing (e.g. painting).

Over-fluxing can lead to more rapid flux build-up on the fixtures and increase the maintenance intervals.

Over-fluxing is a waste of flux, which will inevitably increase process costs.

While “more flux is better” is true in some circumstances, there is an overwhelmingly negative impact from increasing the flux load to compensate for some process deficiencies.
Flux Slurry Concentration is the Only Factor to Control Flux Load

As a flux producer and supplier, Solvay has received many enquiries over the years asking what slurry concentration should be used to achieve the optimum flux load on a part to be brazed. This specific request is related to the belief that flux slurry concentration is the only factor controlling flux loading.

There are in fact many other factors affecting flux loading and they must all be taken into consideration when targeting a certain level. First is the application method whether it be dipping, spraying or flooding. Even the type of spray will deposit more or less flux on the component surfaces, depending on nozzle configuration (atomising spray vs. shower effect). The component surface wettability (i.e. the ability of the aluminium surface to be uniformly coated with a water-based flux slurry), conveyor belt speed, and the strength and volume of the air blow-off all play a role in controlling flux loading.

While the flux slurry concentration is important, all these other factors also contribute to control the flux loading. If any one factor is changed, the flux load will change. The goal is to balance all factors to achieve the desired flux quantity on the surfaces.

Diagram 2: NOCOLOK® Flux Slurry – Relationship between Slurry Density and Concentration

\[ \text{Density} = 0.008 \times \text{Concentration} + 0.9893 \]

\[ R^2 = 0.9971 \]
(1) Yamaguchi M., Kawase H., Koyama H. Furukawa, Review No. 12, 1993, p145–149
(4) Steward N. I., Field D. J., SAE 870186, 1987
(5) Lauzon D. C., Belt H. J., Bentrup U., Therm Alliance International Invitational Brazing Seminar, Detroit, 1998
You Want More Information. You’re Welcome:

“The NOCOLOK® Flux Brazing Process” – the complete detailed technical brochure. Available in several languages.


The brochure “The NOCOLOK® Flux Product Stewardship Concept”. Available in several languages.

“Flame Brazing with NOCOLOK® Flux” – the complete detailed technical brochure. Available in several languages.

The compendium on CD-ROM: With the NOCOLOK, Flux Dictionary, all print publications and the NOCOLOK® Flux Multimedia Show.

The video “NOCOLOK® Flux – The Brazing Story”. Interesting and informative.

The video “Live on stage – The Solvay Brazing Seminar”.

The video “Flame Brazing”.

Your Contact to NOCOLOK® Flux

Marketing:
Telephone  +49-(0)5 11-8 57-0
Telefax   +49-(0)5 11-8 57-21 46

Technical Service:
Telephone  +49-(0)5 11-8 57-0
Telefax   +49-(0)5 11-8 57-21 66

Solvay Fluor und Derivate GmbH
Hans-Böckler-Allee 20 · D-30173 Hannover
Telephone  +49-(0)5 11-8 57-0
Telefax   +49-(0)5 11-8 57-21 46
Internet  http://www.solvay-fluor.com

NOCOLOK is registered trademark of Solvay Fluor und Derivate GmbH, Germany

All statements, information, and data given herein are believed to be accurate and reliable but are presented without guarantee, warranty or responsibility of any kind, expressed or implied. Statements or suggestions concerning possible use of our products are made without representation or warranty that any such use is free of patent infringement, and are not recommendations to infringe any patent. The user should not assume that all safety measures are indicated, or that other measures may not be required.