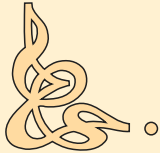
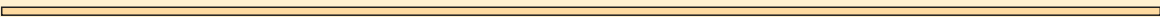


The Myths of NOCOLOK®

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







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

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Introduction



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.

Myth No. 3

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.

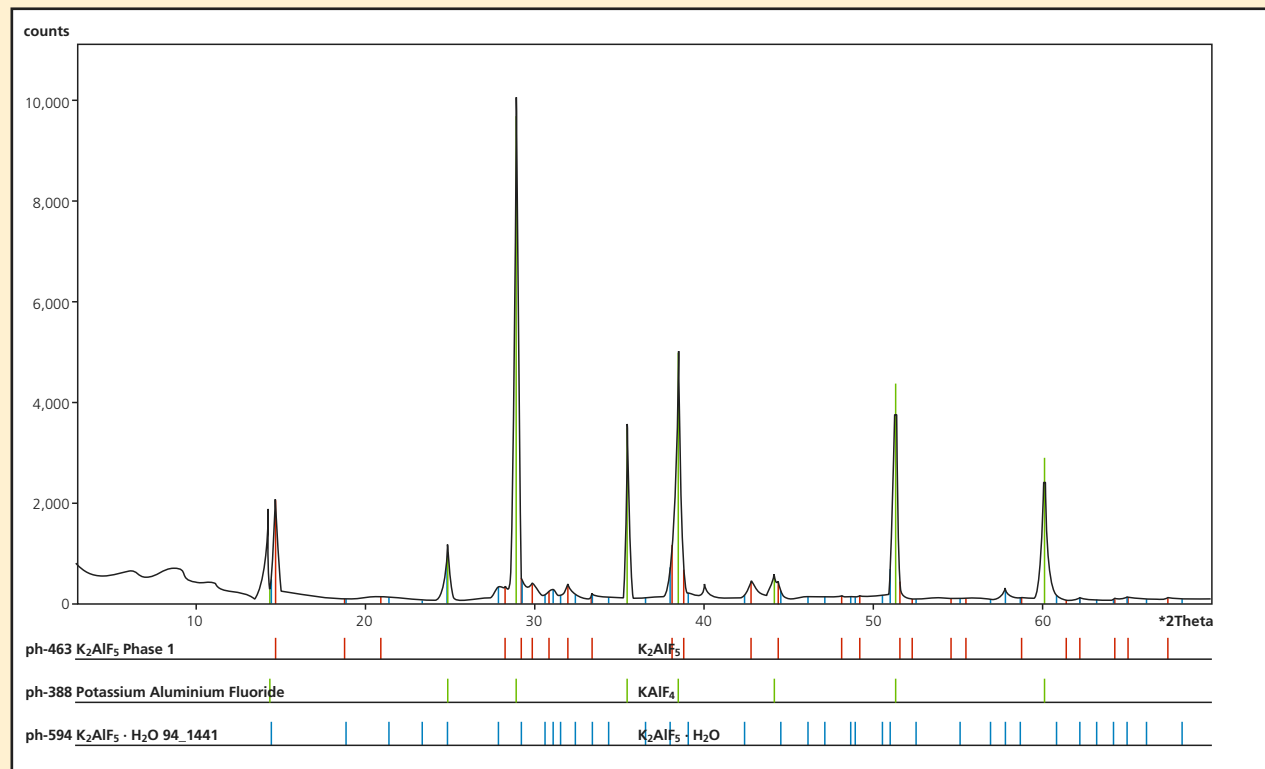


Figure 5: Typical X-Ray Diffraction (XRD) Diagram of NOCOLOK® Flux

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.

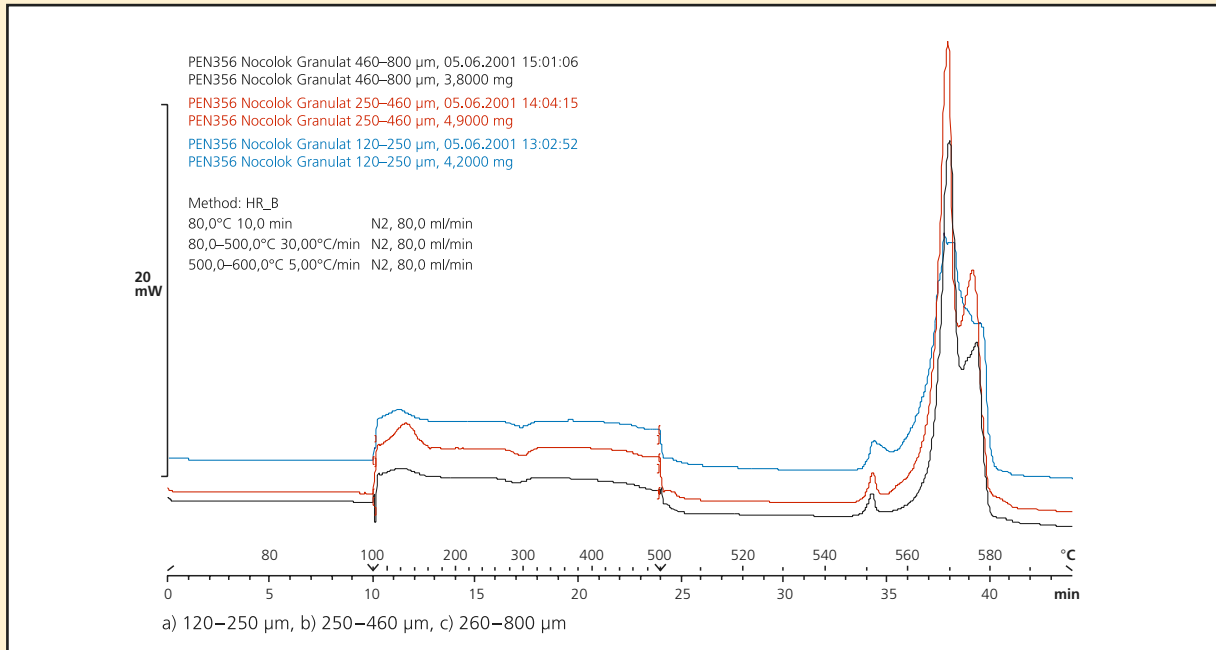


Figure 1: DSC Scans for Granulated NOCOLOK® Flux Samples

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⁽¹⁾. 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

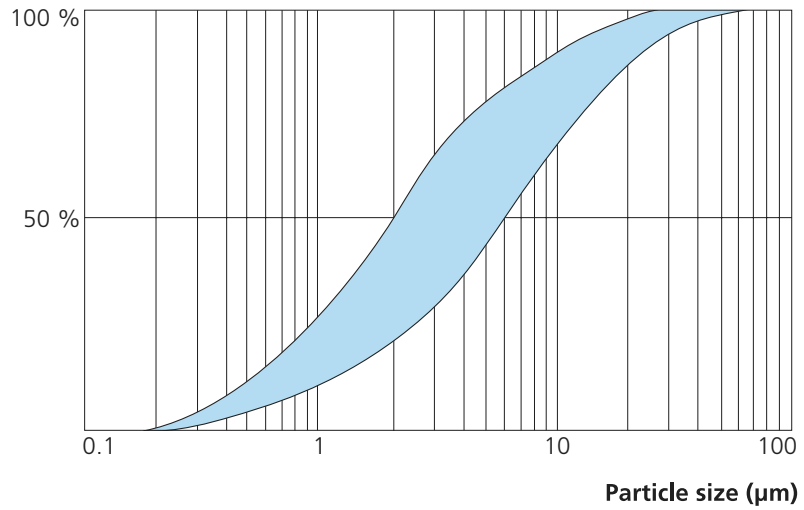
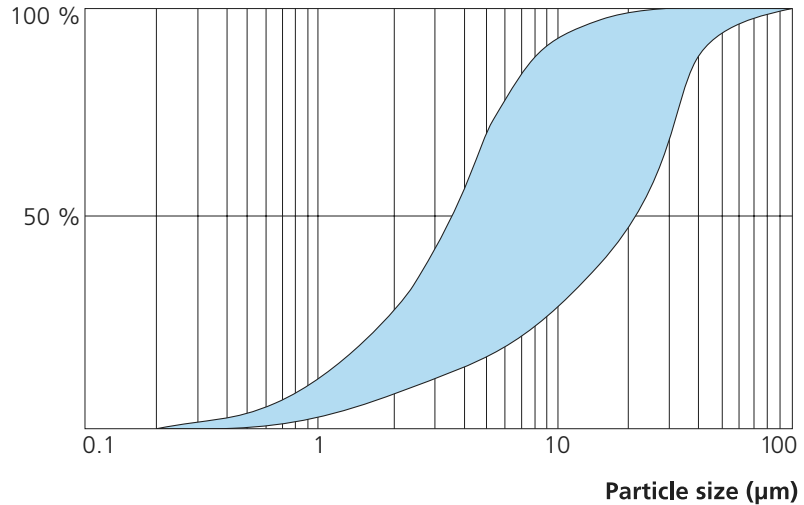


Figure 3:
Typical Particle Size Distribution
for NOCOLOK® Flux Drystatic
(Electrostatic) Application



Fluxes With a Lower Melting Range are Superior



here 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 – $KAlF_4$ – begins progressively evaporating, with a vapour pressure determined to be 0.08 mbar at 600°C⁽²⁾. Evaporation of $KAlF_4$ 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:

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

Table 1: What Takes Place During Brazing?

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 K_2AlF_5 content, the flux will start to melt at a lower temperature so that the flux will

work at a lower temperature. However, even if $KAlF_4$ evaporation is ignored, the same study concluded that increasing the K_2AlF_5 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



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

$K_{1-3}AlF_{4-6}$. 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.

Although there are several brands of non-corrosive aluminium brazing fluxes, at brazing temperature, they are all understood to be a mixture of $KAlF_4$ and K_3AlF_6 . When heated up to brazing temperature, one of the flux components ($KAlF_4$) 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 $KAlF_4$ 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 $KAlF_4 - K_2AlF_5 \cdot H_2O$ 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 %.

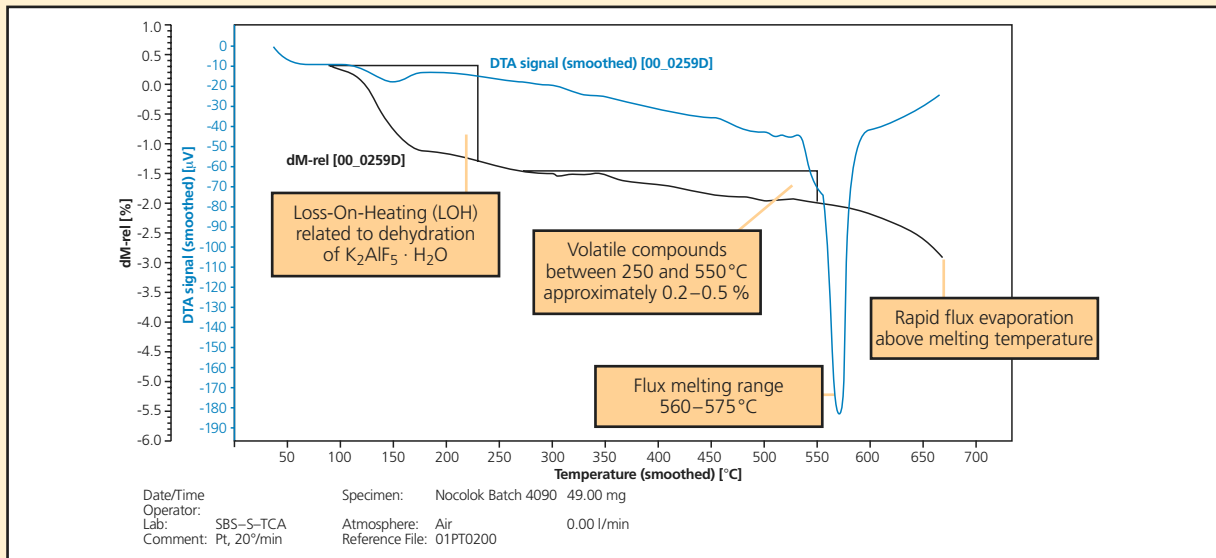
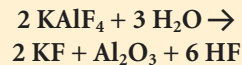
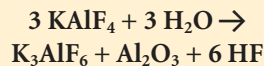


Figure 4: Differential Thermal Analysis (DTA) Diagram for NOCOLOK® Flux (Batch 4090) – Heating Rate 20 °C/Min

Myth No. 3

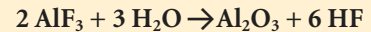
It is clear that all fluxes will create flux fumes, with strong evidence suggesting that the vapour primarily contains KAlF_4 . With regard to CAB brazing (furnace brazing) where traces of moisture are always present even at -40°C dew point (which corresponds to 106 ppm H_2O at atmosphere pressure), a number of compounds can be formed in the system $\text{K} - \text{Al} - \text{F} - \text{H} - \text{O}$. 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:



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 AlF_3 dissolved in the flux melt is subject to hydrolysis according to:



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.

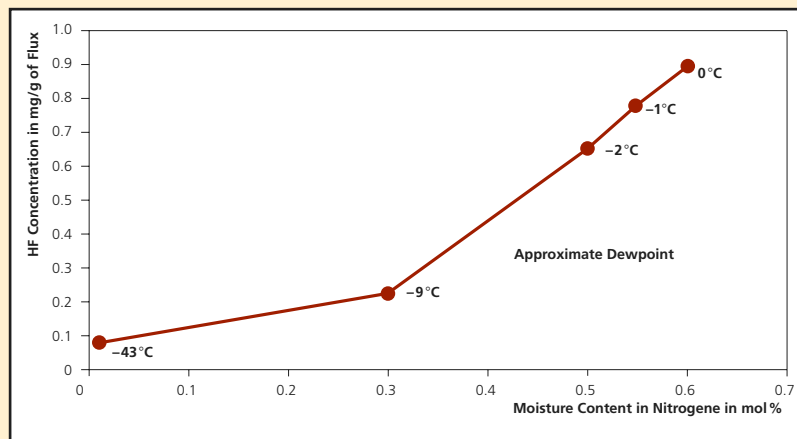


Diagram 1: HF Generated as Function of Moisture Content⁽⁵⁾

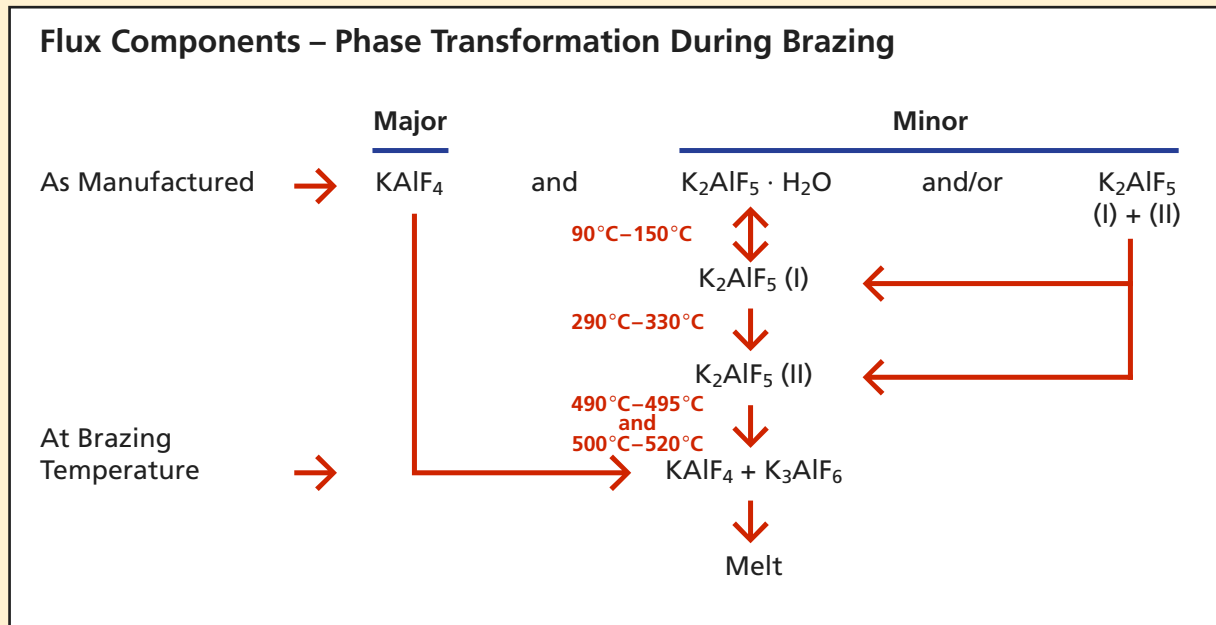
“Pure” Flux Compounds (i.e. “Pure” Fluxes) are Better for Brazing



Some believe that pure flux phases such as pure $KAlF_4$ or K_2AlF_5 are better for brazing than mixtures of phases. Some have even referred to the presence of K_2AlF_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_2AlF_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_2AlF_5 was used. Furthermore, the presence of

K_2AlF_5 is necessary to achieve the proper ratio of $KAlF_4$ and K_3AlF_6 at brazing temperature, the necessary condition to form the eutectic. This can be explained more thoroughly by examining the following schematic:



As manufactured, a flux typically contains a mixture of $KAlF_4$ and K_2AlF_5 , where the K_2AlF_5 may or may not be hydrated (see **Figure 5**: “Typical XRD Diagram of NOCOLOK® Flux”). During the

brazing process, the material undergoes essential physico-chemical transformations. While the chief component, $KAlF_4$, is simply heated up, the compound $K_2AlF_5 \cdot H_2O$ 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°C–330°C, two different crystallographic modifications of K_2AlF_5 are formed⁽⁶⁾. When the furnace temperature is raised above 490°C, K_2AlF_5 begins to dissociate:



The exact amount of K_3AlF_6 necessary for a eutectic flux composition is obtained from the original K_2AlF_5 content. It is the ratio between the total amount of $KAlF_4$ (as manufactured and dissociation of K_2AlF_5) and K_3AlF_6 that forms the basis for flux melting.

In fact, the flux manufacturer chooses the ratio of $KAlF_4$ and K_3AlF_6 based on the eutectic AlF_3 -KF phase diagram (see left), which was first constructed in 1932⁽⁷⁾ and further researched and refined in 1966⁽⁸⁾.

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.

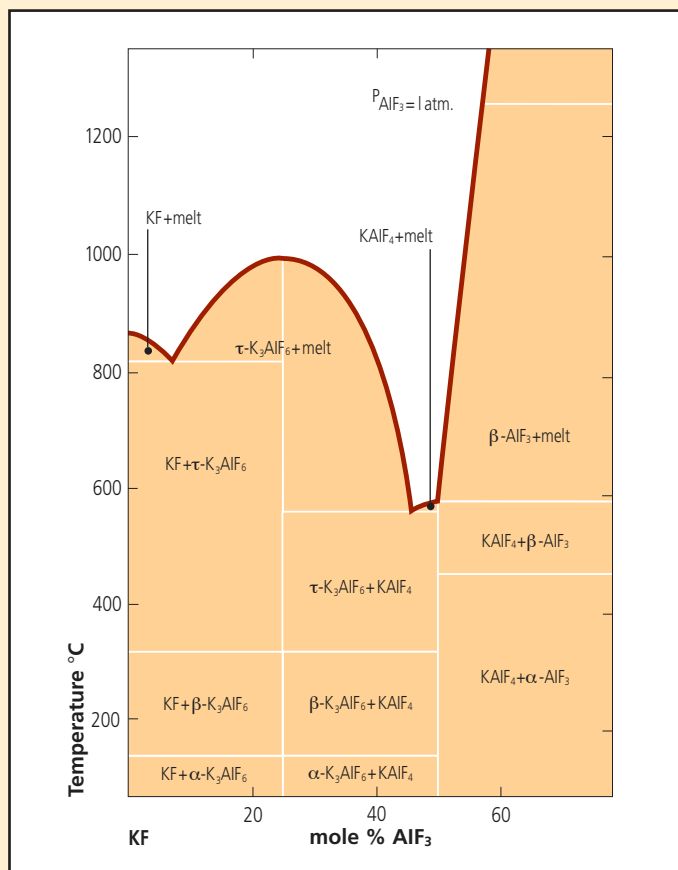


Figure 6: Melting Phase Diagram for the Potassium Fluoride (KF) – Aluminium Fluoride (AlF₃) System

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



hemicals (solid or liquid, inorganic and organic substances) are hygroscopic when they attract moisture while stored in – or exposed to – air where traces of humidity are always present. Consequently, hygroscopic liquid chemicals (e.g., sulphuric acid, glycerine, alcohol, etc.) become diluted, while hygroscopic solid materials begin agglomeration and become liquified. Hygroscopic solids are mainly salts that are highly soluble in water (e.g. $MgCl_2$, $CaCl_2$, P_4O_{10} , etc.). Their saturated solutions have a low water vapour pressure because of the high salt concentration. Water vapour from surrounding air condenses on the salt, resulting in a saturated solution. The salt starts to liquify, i.e. it 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 ad-

sorption 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 (de-sorption) 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.

The only interaction of NOCOLOK® Flux with moisture is the re-hydration of phase I K_2AlF_5 to $K_2AlF_5 \cdot H_2O$. In the drying step of the NOCOLOK® Flux production, most of the $K_2AlF_5 \cdot H_2O$ is converted into K_2AlF_5 phase II. K_2AlF_5 phase II does not pick up water molecules from air, and under these conditions will not transform to K_2AlF_5 . Traces of phase I K_2AlF_5 present in the flux will most likely re-hydrate within six months after production. The total difference of loss-on-heating analysis related to the re-hydration of phase I K_2AlF_5 after this period is on average 0.5 %, without affecting the visible material appearance. As far as we know, there is no change in any chemical or physical flux characteristic related to this effect.

Adsorption of moisture under humid conditions is an absolutely normal physical effect for a powder with large surface area. The flux has a very low water solubility and it will not liquefy in air by attracting humidity. NOCOLOK® Flux does not chemically react with moisture, and thus is not hygroscopic!

More Flux is Better



his is another myth – although there can be some truth to it. But all the specifics must be considered before accepting the simple statement that more flux is better.

In heat exchanger problem areas such as in tube-to-header joints or where Mg-containing alloys are used, it is common practice to increase the flux loading. Dual concentration fluxing stations (where one concentration of flux slurry is used for the fin pack and a higher concentration for the tube-to-header joints) are still common. Manual flux application where 6XXX series alloys are used for fittings is also common practice. In these cases, more flux is better because it promotes maximum filler metal flow to critical joint areas while minimising exposure to furnace

atmosphere contaminants. When higher Mg-containing alloys are used, higher flux loads can compensate for faster re-oxidation rates, and for the chemical interaction between magnesium and fluoride.

In most cases, though, more flux is used to mask furnace atmosphere or heat exchanger design deficiencies such as poor component fit-up. Flux is frequently seen as a cure-all bandage. While this is often the case, it should only be used in this fashion temporarily, until the real issues are resolved.

Over-fluxing leads to the generation of more effluent where condensed $KAlF_4$ vapours will load up the dry scrubber more quickly. Continuous drips on the furnace floor caused by over-fluxing can lead to an accumulation of flux, which can eventually deflect the mesh belt or prematurely corrode the muffle.

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.

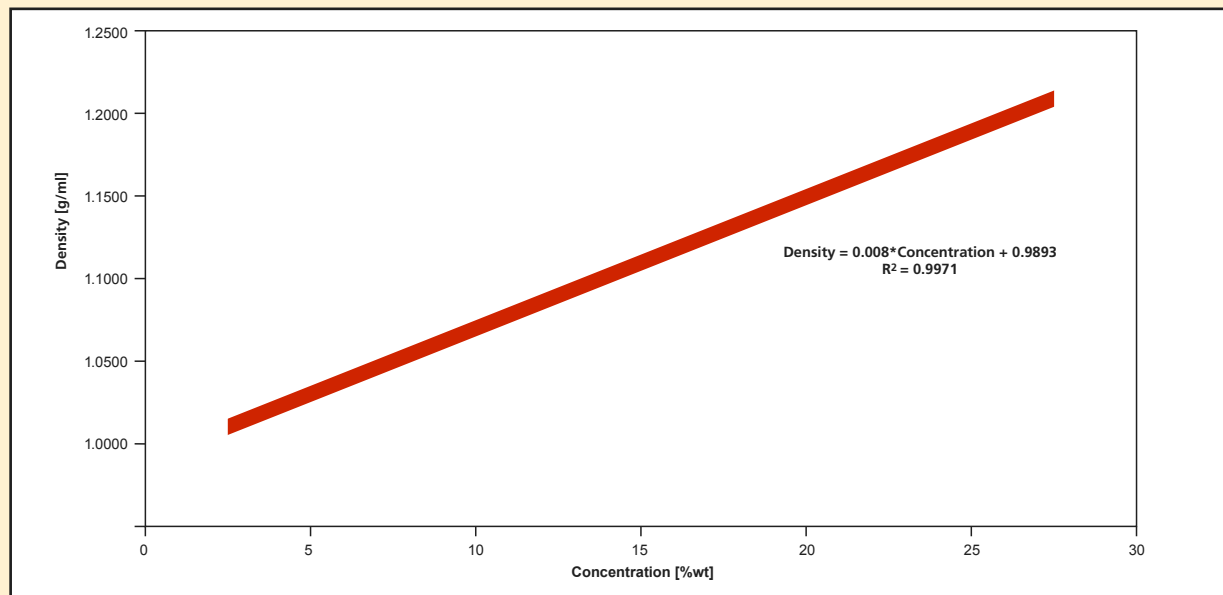


Diagram 2: NOCOLOK® Flux Slurry – Relationship between Slurry Density and Concentration



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More Information

You Want More Information. You're Welcome:



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



“The Technical Brazing Centre” –
NOCOLOK® Flux Brazing Services.
Available in several languages.



The brochure “The
NOCOLOK® Flux Product
Stewardship Concept”.



“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”.

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NOCOLOK® Flux

Right to the point!

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