

HF Generation in NOCOLOK™ Flux Brazing Furnaces

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ABSTRACT

The NOCOLOK flux brazing process is now accepted worldwide for the manufacturing of aluminum heat exchangers. The purpose of the flux is to remove the oxide film from the metal surface and promote filler metal wetting and flow. Since the flux is a mixture of fluoride containing salts, it can react with moisture from the brazing atmosphere to produce the corrosive HF gas.

This paper describes the experimental procedure to show the importance of dewpoint control to minimize the formation of HF gas. Samples of flux were heated and melted in a laboratory furnace under flowing nitrogen doped with various moisture contents. The nitrogen gas flowing out of the furnace was dispersed in a buffered aqueous solution which dissolved all fluoride containing compounds. A fluoride selective electrode was used to monitor the fluoride concentration in the solution. The amount of HF generated by the flux at different dewpoints was determined.

In order to lay a foundation for the basic understanding of HF generation, this paper further describes possible reaction mechanisms based on available thermodynamic data.

INTRODUCTION

There is a considerable amount of information published on NOCOLOK flux brazing which describes many aspects of the process. However there is very little practical information about the consequences of altering process variables such as dewpoint. It has always been known that a high dewpoint in the critical brazing zone of the furnace can certainly affect component reject rates. Another equally known consequence and the focus of this paper is the increase in concentration of the corrosive gas hydrogen fluoride or HF.

NOCOLOK flux is an inorganic fluoride salt consisting of the general formula $K_{1-3}AlF_{4-6}$. Fluxes in this family are considered intrinsically non-corrosive in that they are non-hygroscopic, they do not react with Al whether the flux is solid or molten and can remain on the surface of the brazed component as a thin tightly adherent inert residue.

All fluxes in this family have a tendency to react with furnace atmosphere moisture to produce HF where the moisture content or concentration is almost always expressed as dewpoint. Figure 1 shows that the relationship between dewpoint and moisture concentration is not linear. If one assumes the recommended dewpoint for NOCOLOK flux brazing to be -40°C , the corresponding moisture concentration is $0.08\text{ g H}_2\text{O/kg dry air}$. Increasing the dewpoint to -30°C represents a threefold increase in moisture content ($0.24\text{ g H}_2\text{O/kg dry air}$). At -20°C dewpoint, there is almost an eightfold increase in the moisture content ($0.63\text{ g H}_2\text{O/kg dry air}$) compared to -40°C dewpoint. These values are indicated to show that small changes in dewpoint correspond to significantly higher moisture contents available to react to form HF.

The formation of HF in controlled atmosphere brazing furnaces is often cited as one of the leading causes of furnace muffle and furnace mesh belt corrosion. It is therefore the intention of this paper to show a relationship between moisture content (dewpoint) and the amount of HF generated.

EXPERIMENTAL PROCEDURE

The purpose of this work is to quantify the amount of HF generated as a function of furnace atmosphere dewpoint. In production, the flux is mixed with water as a suspension and sprayed onto the components to be brazed. The components then travel on a belt first through a drying furnace to remove water from the fluxing operation. The temperature here is usually about 200°C to 250°C . The components then travel through the nitrogen atmosphere brazing tunnel furnace through a series of heating zones until the final brazing temperature of about 600°C is reached. The heating rate is $> 20^{\circ}\text{C/min}$. The components are then cooled until the flux and filler metal is solidified, also in a nitrogen atmosphere. The experimental procedure used for the measurement of HF attempts to reproduce these process parameters.

Test Apparatus

Figure 2 shows a schematic of the test apparatus used in this experiment. The test set-up consists of a stainless steel muffle furnace capable of heating 3 flux samples simultaneously. Nitrogen flows through the furnace and the effluent passes first through a safety flask then into a buffered acetate solution. The fluoride ion concentration in the buffered solution is measured with a fluoride sensitive electrode.

Flux Sample Preparation

For each test run, 0.333 g of flux was measured out into 3 small Al pie-plate containers for a total of 1 g of flux per test run. Each sample of flux was dispersed in 6 ml of water. The samples were then dried at 600°C for 18 hours (overnight). Just prior to the test run, the flux's crystalline water was removed by increasing the temperature of the drying furnace from 60°C to 200°C over a period of 2 hours.

Test Procedure

The 3 flux samples comprising one run were placed side by side in the stainless steel tube furnace. When the furnace was hermetically sealed, the thermocouple

was placed in the middle of the furnace. The furnace was then purged for 20 minutes with dry nitrogen flowing through a molecular sieve at 15 l/h.

The nitrogen source was switched to that with the defined moisture content keeping the flow rate at 15 l/h. The temperature was increased at a ramp rate of 20°C/min. up to the target temperature of 600 °C. The samples were then allowed to dwell at 600°C for 15 minutes followed by a 60 minute cool down period. During the first 15 minutes of the cool down period the furnace was purged with the nitrogen containing the defined moisture content and followed with dry nitrogen for the last 45 minutes. The test parameters are summarized in Figure 3.

The nitrogen effluent from the furnace was first passed through a safety flask then through 2 acetate buffered solutions. Any F containing effluent not completely dissolved in the first buffered solution was expected to be dissolved by the second buffered solution. The fluoride ion concentration was measured from the combined buffering solutions.

Quantitative Analysis of Fluoride in the Buffered Solutions

The quantitative analysis of the dissolved fluorides was accomplished with a fluoride selective electrode. Prior to each measurement the electrode was calibrated against standard solutions. As stated above, the nitrogen effluent from the furnace was passed through 2 buffered solutions. The purpose of buffering the solution is to decomplex Al and F ions and to maintain a stable pH so as to not influence the fluoride selective electrode. A master solution was prepared for this purpose and consisted of 164.1 g/l dehydrated sodium acetate, 396.0 g/l sodium nitrate and 8.0 ml/l acetic acid. The buffering solutions were then prepared by taking a 15 ml aliquot of the master solution and diluting it to 250 ml with water.

The fluoride ion concentration measured by the electrode is for total F. It is assumed that the F will enter the buffering solutions either as HF and/or KAIF_4 vapor (see discussion). In order to subtract the contribution from KAIF_4 in the total F content, the Al concentration in the post-test solution was analysed by the inductively coupled plasma technique (ICP). The fluoride concentration, ignoring the contribution from KAIF_4 , and the amount of HF per gram of flux could thus be calculated.

Determination of Water Content in the Nitrogen Gas

During the simulated braze cycle, the furnace was purged with dry nitrogen (over a molecular sieve) as well as with nitrogen with defined moisture contents. Nitrogen gas with 100 ppm H_2O (0.01 mol%) was available commercially.

The higher moisture content gases were prepared by bubbling nitrogen through ice water and room temperature water at 15 l/h for a certain period of time in order to become moisture laden. The moisture content was then determined by passing the moisture laden nitrogen through a cold trap (ethanol with dry ice or liquid nitrogen).

RESULTS AND DISCUSSION

The ion selective electrode measures the total amount of fluoride in solution. It is assumed that the F enters the buffering solution as HF or KAIF_4 . The KAIF_4 is de-

complexed by the buffering solution which allows the total F content to be measured. It is assumed of course that not all of the KAlF_4 generated during the simulated braze cycle will enter the buffering solution. Since KAlF_4 is a vapor, some of it may condense on the colder parts of the system and some of it will be carried into the buffering solution. The F component that does enter the buffering solution as KAlF_4 is therefore subtracted from the total F content. The final HF concentration expressed as mg per gram of flux is thus calculated from the remaining F.

The test runs with the dry nitrogen showed that the F concentration from KAlF_4 to be 0.14 mg/g of flux. For the moisture contents of 0.30 mol%, 0.50 mol%, 0.55 mol% and 0.6 mol%, the F contribution from KAlF_4 was remarkably constant at 0.20 mg/g of flux. For reasons beyond our control, the Al content in the buffering solutions from the test runs containing 0.01 mol% and 1.5 mol% moisture were not available. Considering the consistency of the F from KAlF_4 in the solutions which were analysed, the authors assumed a value of 0.20 mg F/g of flux for the other two solutions (shown in Table 2 with an asterix).

Table 2
HF Concentration as a Function of Moisture Content

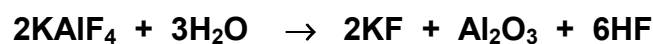
Moisture Content in N_2 (mol%)	Total Fluoride (mg/g of flux)	Fluoride from KAlF_4 (mg/g of flux)	Fluoride from HF (mg/g of flux)	HF Concentration (mg/g of flux)
0	0.17	0.14	0.03	0.04
0.01	0.28	0.20*	0.08	0.07
0.30	0.54	0.20	0.34	0.35
0.50	0.80	0.20	0.60	0.63
0.55	0.93	0.20	0.73	0.77
0.60	1.05	0.20	0.85	0.89
1.50	2.29	0.20*	2.09	2.20

The results from Table 2 are shown graphically in Figure 4 along with the corresponding approximate dewpoints. The HF concentration for the 1.5 mol% moisture content is not shown. The trend is obvious; the higher the moisture content, the more HF is generated. For a couple of reasons, no correlation was attempted. First of all, although the process and brazing conditions were simulated as best as possible, there are still too many unknowns (phase stabilities, actual mechanism of HF generation, etc). Secondly, there is not enough data in the actual brazing dewpoint regime. That is, additional data in the area of -40°C to 0°C would be required to propose a correlation. This was not possible in our investigation due to the difficulties in doping nitrogen with very low levels of moisture accurately and reproducibly.

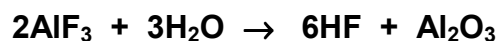
It has always been recommended to braze at a dewpoint of -40°C to minimize the amount of flux and to minimize the amount of HF generated. Our investigation shows that a dewpoint of -43°C produces nearly the same amount of HF as when bone-dry nitrogen is used (as shown in Figure 4). This provides confirmation, at least from the point of view of HF generation, that -40°C is a realistic recommendation.

This leads to the obvious question of how HF is generated even if bone-dry nitrogen is used. Our work showed that dry nitrogen still produced 0.04 mg of HF per gram of flux. If HF is to be generated, there must be other sources of moisture contamination. This might include reduction of aluminum oxides, degassing of furnace walls, leakage and other less obvious sources. The fact is, it is virtually impossible to avoid some HF formation, even under the best of conditions.

Thompson and Goad (1) have studied the thermodynamic properties of flux melts and have determined that the KAIF_4 component of the flux has a significant vapor pressure at brazing temperature (0.08 mbar @ 600°C). It is presently believed by the authors that the most likely means of HF generation is the reaction of KAIF_4 vapor with H_2O gas:



Thompson and Goad did not propose the above reaction as a mechanism for the formation of HF, but rather proposed that the AlF_3 dissolved in the flux melt is subject to hydrolysis and may react with water vapor according to:



From the proposed mechanisms, it is logical to assume that the nitrogen effluent should also contain Al_2O_3 and/or KF. However Solvay Fluor und Derivate have never detected these compounds in KAIF_4 condensates and therefore assume that if they are formed, the quantities are negligible. It is for this reason that the authors have considered only KAIF_4 and HF as the compounds which could enter the buffering solutions.

Many other compounds and phases could exist. It is impossible to predict with certainty which compounds will and will not exist and in what temperature and partial pressure of water regimes. Any number of reactions can be written, but until more is known about the phase stabilities of this complicated system, it cannot be said with certainty whether any particular reaction occurs.

CONCLUSIONS

- Increasing the moisture content in nitrogen results in an increase in the concentration of HF generated.
- A dewpoint of -43°C produces nearly the same amount of HF as with the most ideal of conditions.

- Even with dry nitrogen passed over a molecular sieve under controlled conditions, some HF is generated (0,04 mg/ g of flux) indicating that its formation is virtually unavoidable and is attributed to non-obvious sources of moisture contamination.

REFERENCES

1. Thompson, W.T. and Goad, D.G.W., *Some Thermodynamic Properties of K_3AlF_6 – $KAlF_4$ Melts*.
Can. J. Chem., 1976 **54** p. 3342-3349.

Figure 1
Relationship Between Dew Point and Moisture Content

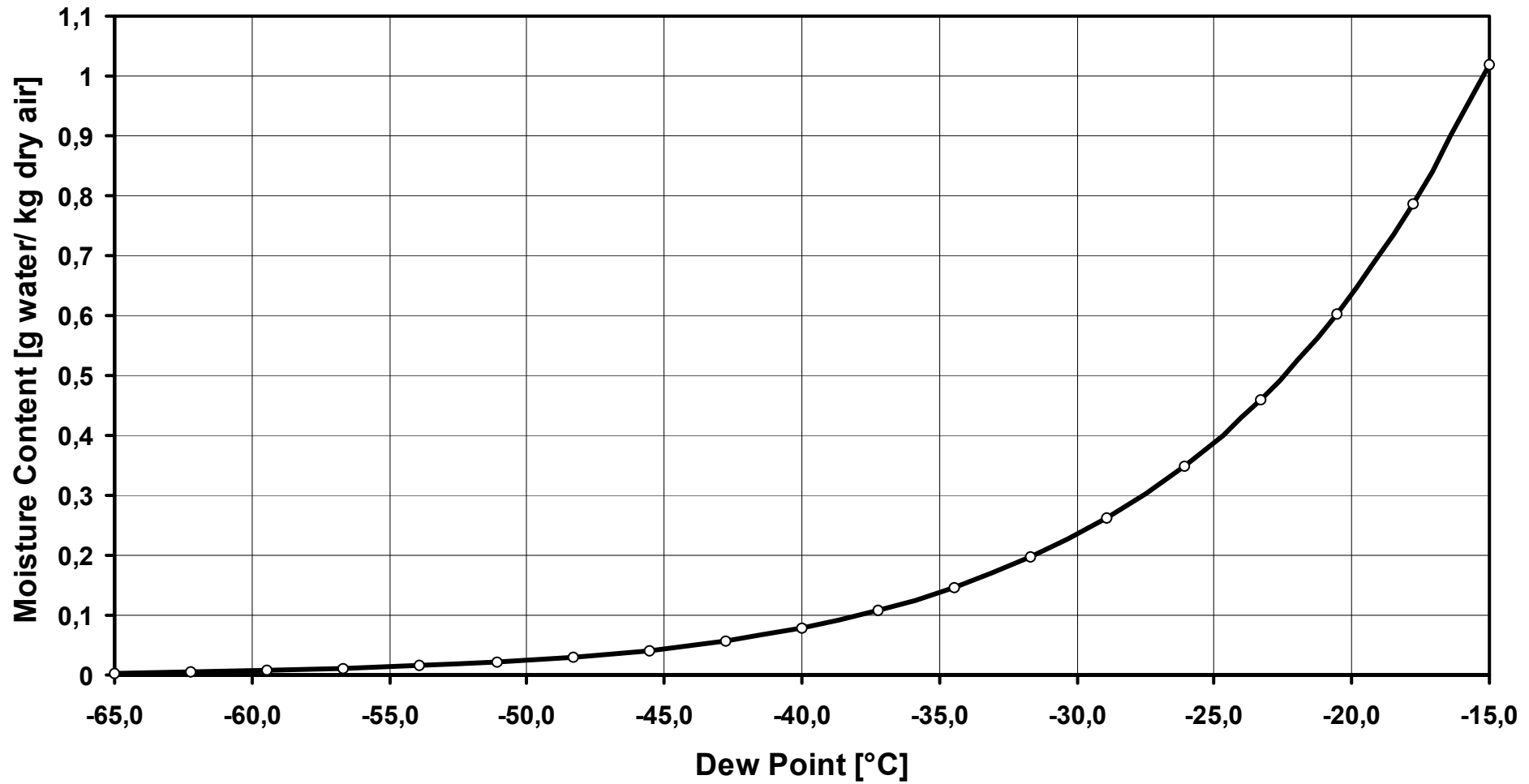


Figure 2
Test Apparatus

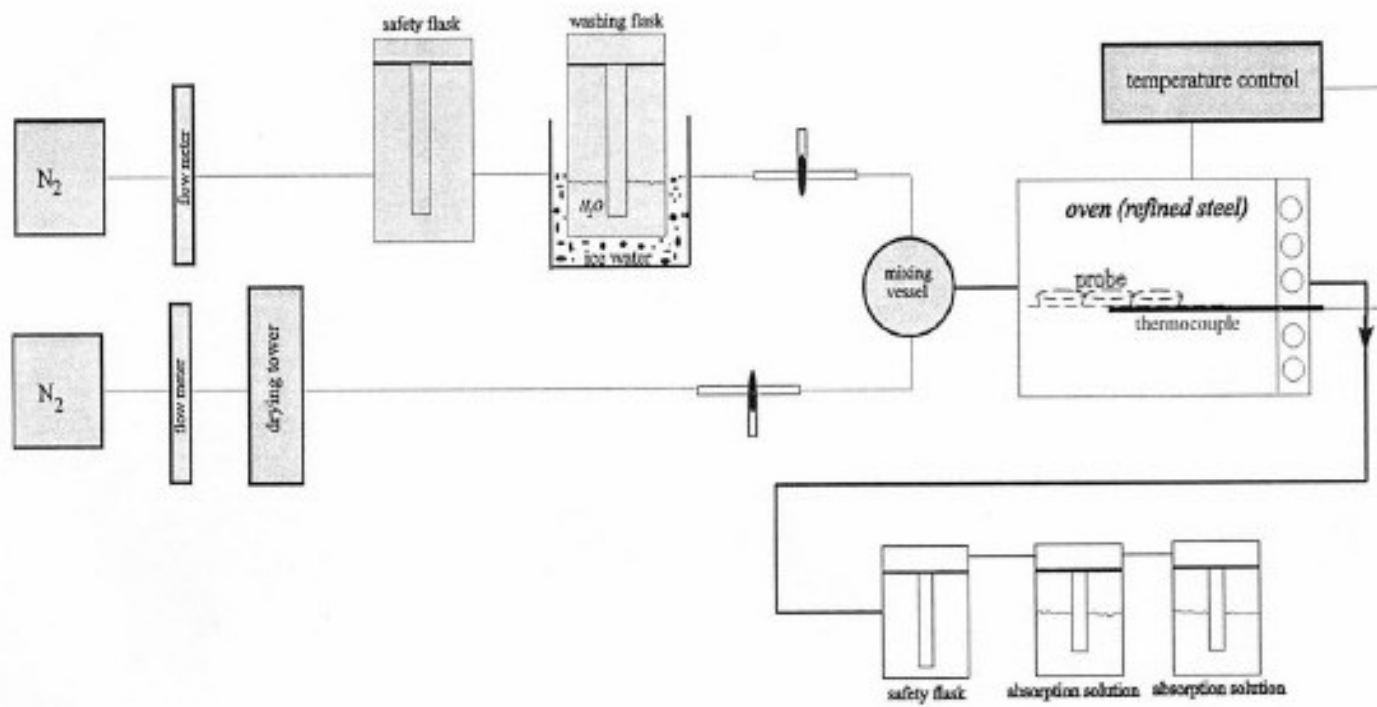


Figure 3
Test Parameters

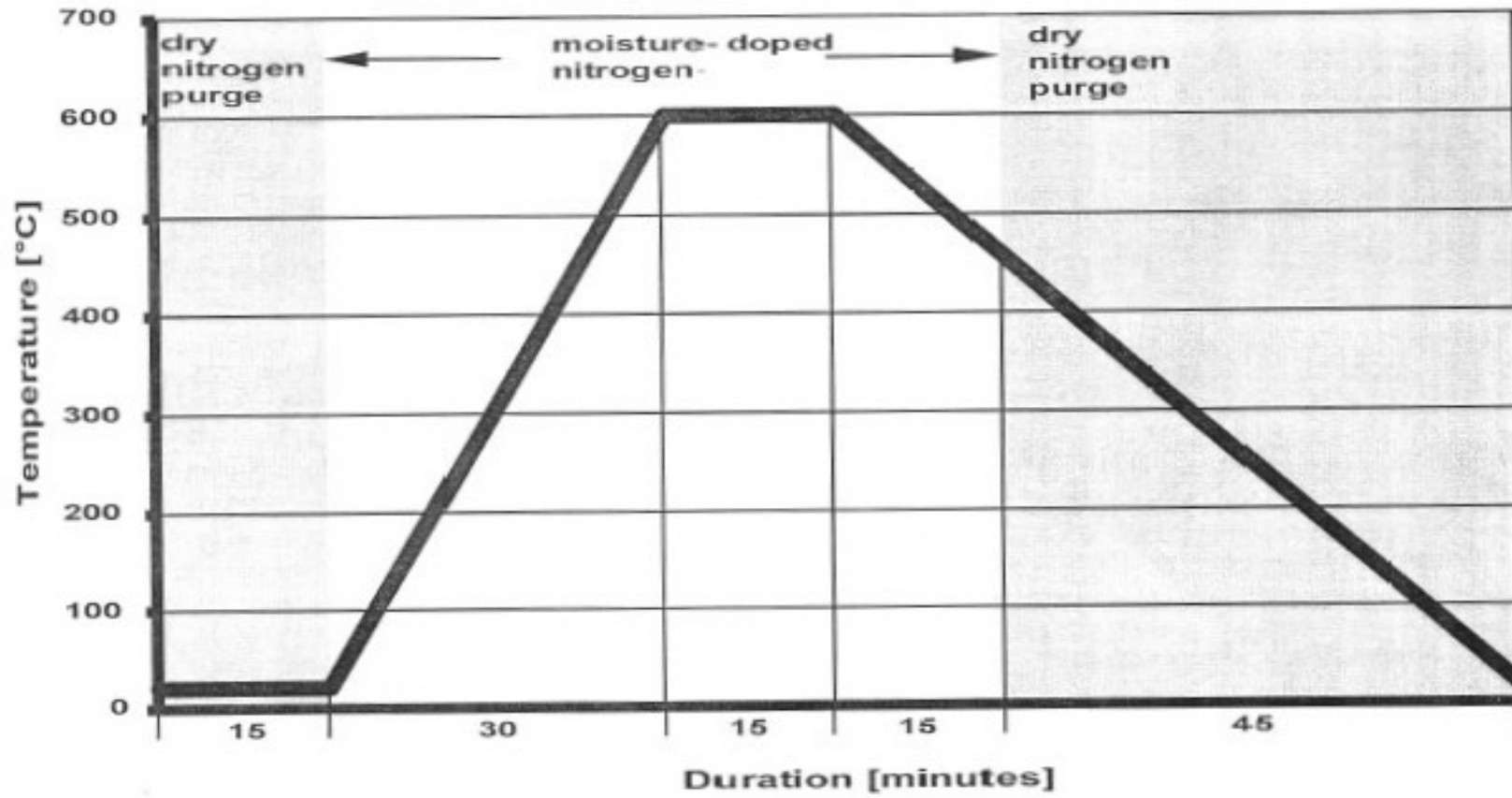


Figure 4
HF Generated as a Function of Moisture Content

