DISTRIBUTION OF AMINES AND ORGANIC ACIDS IN THE SECONDARY SIDE OF EMBALSE NUCLEAR POWER STATION

H.R.CORTI[1], R.JIMENEZ REBAGLIATI[1], N.FERNANDEZ[2] and W.ALLEMANDI[2]

ABSTRACT

In this work we summarized the distribution of amines and organic acids generated by the thermal decomposition of morpholine in the secondary side of Embalse NPP. Sampling and analytical procedures to determine the concentration of formic, acetic and glycolic acids, morpholine, ammonia, methylamine, ethanolamine and 2(2-aminoethoxy)ethanol are described. Two sets of samples were collected in March 1995 and October 1996 in the following points: main steam line, composite steam generator blowdown, moisture separator, condensate extraction pump discharge and outlet feed pump.

The general trend of the product distribution along the secondary side is similar to that reported for other CANDU NPP. In CNE methylamine and ethanolamine are more abundant than 2(2-aminoethoxy)ethanol due to faster decomposition of morpholine and less oxidizing conditions. Ammonia, and methylamine concentrate in the steam because of the lack of a de-areator. The volalitilty of ethanolamine is low and its concentration in the steam generator is high. It could help to neutralize acid conditions in crevices and sludges.

The concentration of organic acids in CNE is low as compared with other CANDU NPP, with formic acid being the predominant species. Differences in the relative concentrations of morpholine degradation products as compared to other CANDU NPP are discussed.

1) Unidad de Actividad Química, Centro Atómico Constituyentes, C.N.E.A.
2) Central Nuclear Embalse, Nucleoeléctrica Argentina S.A.

DISTRIBUTION OF AMINES AND ORGANIC ACIDS IN THE SECONDARY SIDE OF EMBALSE NUCLEAR POWER STATION

H.R.CORTI, R.JIMENEZ REBAGLIATI, N.FERNANDEZ and W.ALLEMANDI

INTRODUCTION

Embalse NPP has been running under all volatile chemical treatment (AVT) in the secondary side since it started up in 1984. This treatment uses morpholine to keep the acidity of feedwater within specification (pH=9.3), while the oxygen concentration is kept below 5 ppb by adding hydrazine.
Both additives are decomposed under the temperature conditions of the secondary side yielding volatile products which are distributed throughout the secondary system. Hydrazine produces ammonia while morpholine suffers complex reactions which lead to the formation of amines, alcohols, and organic acids with different volatilities. The distribution coefficients of ammonia and morpholine between water and steam have been measured at high temperature [1,2] but there is a lack of information on the distribution coefficients of the degradation products of morpholine, which prevent assessing their concentrations in different parts of the secondary side.
Although the operational experience of the secondary side of Embalse NPP has been good [3], a better understanding of the secondary side chemistry requires knowledge of the distribution of these degradation products. The aim of this work is to characterize these chemicals, to measure their concentration in different points of the secondary side, to estimate their effect on the system chemistry and to compare with results reported in other CANDU power stations.

SAMPLING AND ANALYTICAL DETERMINATIONS

Two different sets of samples were taken over two day periods: March 28 and 29, 1995 and October 9 and 10, 1996. Both of them were carried out at five points as indicated in Figure 1, namely: 1) Moisture separator, 2) Main Steam, 3) Combined steam generator blowdown, 4) High pressure heater outlet, 5) Condensate pump discharge. One sample of feedwater and others from the morpholine and hydrazine injection reservoirs were included in the second set of samples.
Two samples were taken at each of the five sampling points, one to determine anions of organic acids by high performance exclusion ionic chromatography, and the other to determine amines by high performance liquid chromatography.
The organic anions were concentrated *in situ* with anionic exchange resin (Lewatit M500-KR), and then eluted with a solution of sodium carbonate 0.12 M to get final concentrations in the range of ppm.
The eluted fractions were analyzed by anionic exclusion chromatography, and the three species acetate, formate and glycolate were measured. Because conventional chromatography was not able to separate these species [4], Ion Chromatography Exclusion (ICE) [5] has been employed successfully to analyze samples for organic acids. ICE separations are based on the species ability to penetrate into the interior of hydrogen form cation exchange resin beds as opposed to the selectivity which governs conventional ion chromatography separations. Stronger acids are excluded from entering the resin beds and therefore they move rapidly through the ICE column. Because of the low flow rates (0.9 cm^3/min) employed in ICE separations, analysis times of 30 minutes or longer are typical for the species of interest.
A solution of sulfuric acid adjusted to pH=3 was used as eluent in isocratic mode. A Varian 5000

Because of the low flow rates (0.9 cm^3/min) employed in ICE separations, analysis times of 30 minutes or longer are typical for the species of interest.

A solution of sulfuric acid adjusted to pH=3 was used as eluent in isocratic mode. A Varian 5000 chromatograph with a loop of 200 µl and an anionic exclusion column Wescan 296/006 with a Peaksimple II data adquisition system were employed.

The samples for the determination of amines were concentrated by a factor 20 by evaporation, after adjusting their pH to 4.0 with 0.1 M HCl to avoid volatilization. Then, they were derivatized with dabsyl chloride (4-dimethylaminoazobenzene-4'-sulphonyl chloride) [6,7] at pH= 9.4 with a solution of sodium bicarbonate and kept in the dark for a minimun of 12 hours. Finally, the resulting precolumn derivatives were filtered through Nucleopore 0.45 µm and injected into a 3900 Hewlett-Packard liquid chromatograph. The time lag between samples was 50 minutes.

Ammmonia, ethanolamine, metylamine and morpholine were detected, separated and quantified using an UV-visible detector at 454 nm, a column Hypersil 100x4,6 mm reverse phase device and mixtures of methanol-water as eluent. Ethylamine was not found in either samplings and in the second sampling, ethanolamine could be separated from 2-(2 aminoethoxy)ethanol [8].

RESULTS

Table I shows the amine concentrations for both sets of samples. The samples taken on March 28, 1995 correspond to plant operation with 6.3 ppm of morpholine in the feed water, which was increased to 7.9 ppm on March 29. The morpholine concentration was constant (5.1 ppm) during the 48 hours sampling in October 1996, and consequently the concentrations of degradation products were lower in this case. The concentration of ammonia is much larger than other amines because it is mainly generated during the decomposition of hydrazine.

Table II shows the concentrations of formic, acetic and glycolic acids found. It can be seen that concentrations are greater for the 1996 sampling, when a high concentration of these acids in the feedwater was detected probably because the retention efficiency of these acids by the water treatment plant [12,13] was not high enough. These concentrations in feedwater were expected to vary with the season, weather conditions, and with the state of the water treatment plant. Thus, a sample of feedwater taken in January 1997 had concentrations of organic acids much lower than that found in October 1996, specially for acetic and glycolic acid. This could account for the lack of correlation between the concentration of morpholine and organic acids in the steam generator blowdown sample. This will be discussed later in this work.

Table III shows the concentration of degradation products obtained in the steam generator blowdown at CNE and those found at Gentilly-2 by Gilbert *et al.* and at Bruce A, Darlington A and Pickering B by McKay [14]. Except for Darlington A which operates with ammonia-hydrazine chemistry, the rest of the plants run under morpholine-hydrazine chemistry, although Gentilly-2 changed to a morpholine treatment without any hydrazine injection in 1984.

It is particulary useful to compare with the values found at Gentilly-2, because the same decomposition products were identified and measured. It is possible, by comparing the measurements of October 1996 for CNE and that of Gentilly-2, when morpholine concentrations were very similar, to conclude that the total amount of amines produced at both reactors (Gentilly-2 and CNE) is very similar. While at CNE ethanolamine and methylamine are the most concentrated products in the liquid and vapor phase, respectively, 2-(2 aminoethoxy)ethanol predominates in both phases in Gentilly-2. Moreover, the presence of a de-areator in Gentilly-2 reduces the concentration of the very volatile methylamine.

Formic acid and ethanolamine are the most concentrated organic acid and amine, respectively, in CNE, while in Gentilly-2 the corresponding products are glycolic acid and 2-(2- aminoethoxy) ethanol. Thus, from Figure 2, we conclude that the concentrations of the more advanced products in the thermal degradation reaction of morpholine are higher in CNE than in Gentilly-2. Under steady state conditions and for a given residence time in the secondary side, the concentration of the final products of the chain reaction will increase with the rate of some particular stages of the reaction scheme. For instance, the concentration of acetic acid increases with the rate of ethylamine hydrolisis and ethanol oxidation.

The high concentrations of ethanolamine reported in Pickering B and Bruce A have been attributed to contamination in the addition tanks [14]. This contamination could also account for the presence of 2-(2-aminoethoxy) ethanol, not reported in those NPP.

If the final products of the decomposition reactions shown in Figure 2 are compared, it is found that acetic and glycolic acids are much more abundant in others CANDU NPP than at CNE. The fact that there is a higher concentration of glycolate at Gentilly-2 could be related to the aforementioned kinetic factor and, additionally, to the greater oxidizing conditions in this plant as compared to CNE. Such conditions favour the formation of the final products corresponding to reaction pathway 2 (Figure 2), while the final products of reaction pathway 1 would be predominant at CNE. McKay [14] suggested that the ratio of blowdown glycolate to feedwater morpholine may be taken as an indicator of the oxidizing condition, and is in agreement with our results. The catalytic effects of copper oxides might also affect the kinetics of these reactions [14] and consequently their relative concentrations around the secondary circuit.

The very high acetate concentrations reported at Bruce A [14] are surely related to the high levels of contamination found in the chemical addition tanks. This is certainly true at Darlington A where morpholine has never been used. Thus, the high temperature degradation of morpholine is not the unique source of organic acids in the secondary side.

Table II also shows that at CNE there is a significant concentration of organic acids, especially of formic acid, in feedwater. Probably this is due to low uptake of low molecular weight and non dissociated organic acids by the water treatment plant. This effect is not observed at Gentilly-2 where the concentrations of organic acids in feedwater are less than 2 ppb.

It is clear that the high level of formic acid at CNE, especially if it is compared with other plants, could be explained by the contributions from feedwater and probably some contamination coming from the morpholine and hydrazine addition tanks.

The relative volatility of morpholine and its degradation products can be analyzed in terms of their distribution coefficients between the steam and water phases, defined by [9]:

$$K^{SG} = \frac{C_S}{C_{SGCB}}$$

for the steam generator, and by:

$$K^{HP} = \frac{C_S}{C_{MS}}$$

for the high-pressure turbine. C_S, C_{CSGB} and C_{MS} are the concentration of a given species in steam, combined steam generator blowdown and moisture separator, respectively.

The values obtained from the concentrations reported in Tables I and II are summarized in Table IV. It is observed that for ammonia K^{SG} is greater than two, while K^{HP} is slightly below one The values of K^{SG} and K^{HP} for morpholine are slightly greater than unity in both sampling. These results are similar to that found in other CANDU NPP [9,10,14].

Methylamine is very volatile, with K^{SG} between 1.8 and 2.6, similar to that reported in Gentilly-2 [10]. On the other hand, K^{HP} for methylamine is very close to unity in the moisture separator at CNE, which would indicate that this amine is retained in the moisture separator more efficiently than it is at Gentilly-2.

Analytical separation of ethanolamine and 2-(2 aminoethoxy) ethanol, achieved before the second sampling, allows us to verify that the concentration of 2-(2 aminoethoxy) ethanol in the steam generator is greater than that of ethanolamine. The distribution coefficient K^{SG} of the latter at CNE is 0.20, similar to the value reported for Gentilly-2 [10].

Thus, ethanolamine concentrates in the steam generator, while 2-(2 aminoethoxy) ethanol having K^{SG} and K^{HP} above one, concentrates in the steam. The low concentration of ethanolamine in steam and in the moisture separator prevent reporting reliable results for K^{HP}.

The distribution coefficients for organic acids at CNE exhibits differences with those reported for Gentilly-2. Formate and glycolate are not as concentrated in the steam generators at CNE as is found at Gentilly-2 [10], but the main difference is that while acetate concentrates at the steam generator at CNE, and in other CANDU NPP [14], the results for Gentilly-2 [10] showed an unexpected high volatility of acetate in the boiler.

The distribution coefficients of organic acid in the moisture separator of CNE fluctuates too much from one sampling to other. The values are slightly below and above the unity indicating higher volatilities for the three acids at CNE as compared to other CANDU NPP.

CONCLUSIONS

The distribution of morpholine and its degradation products at CNE follows the same pattern behaviour as at other CANDU NPP.

At CNE, methylamine in the steam and ethanolamine in the liquid phase are more abundant than 2-(2 aminoethoxy)ethanol because the decomposition of morpholine is shifted toward the final products of reaction pathway 1 due to kinetic factors and redox conditions. The most volatile compounds are methylamine and ammonia which concentrate in the steam. Ethanolamine, on the other hand, concentrates in the steam generator and due to its higher concentration could have a beneficial effect in neutralizing the organic and inorganic acids at crevices and sludges [15].

Formic acid is the most abundant organic acid. It is not clear yet if this is due to the faster decomposition rate of morpholine or to contamination in the makeup water and chemical addition tanks. Organic acids are concentrated in the steam generator.

The absent of a de-aerator at CNE makes the concentration of most volatile species, methylamine and ammonia, greater than in other CANDU NPP having deaerator, such as Gentilly-2. This NPP operates with a modified AVT treatment because the de-aeretor works with low oxygen levels whithout the addition of hydrazine, but it is clear that chemical conditions are more oxidizing than at CNE and probably for this reason the reaction pathway 2 is favoured.

The low concentrations of organic acids at CNE as compared to others CANDU NPP is remarkable and it has probably contributed to the 15 years of good operating experience with the steam generators. The secondary chemistry could be even improved if the concentration of formic acid in the makeup water is reduced and, if posible, contamination in additive tanks is controlled. It should be noted that formic acid is the strongest of the organic acids found in the steam generator, making an important contribution to the cationic conductivity of the steam-water cycle. Hence the effect of lake water chemistry and the operation of the water treatment plant on the makeup water quality should be closely monitored.

REFERENCES

1) E.M.Pawlikowski, J.Newman and J.M.Prausnitz; *Phase equilibria for aqueous solutions of ammonia and carbon dioxide.* Ind.Eng.Chem.Process Des.Dev.; **21**, 764 (1982).

2) P.V.Balakrishnan; *Volatility of amines used for water treatment in steam generating systems.* Can.J.Chem.; **56**, 2620 (1978).

3) A.J.G.Maroto, M.A.Blesa, H.R.Corti, M.Chocrón, P.J.Morando and M.Villegas; *Chemical behaviour of the secondary circuit of Argentine power plants and supporting water chemistry research.* Proceedings of the Second International Steam Generator and Heat Exchanger Conference, Toronto (Canada), pag. xxx (1995).

4) R.Gilbert and C.Lamarre. *Thermal Stability of Morpholine Additive in the Steam-Water Cycle of*

CANDU-PHW Nuclear Power Plant. Can. J. Chem. Eng.; **67**, 676 (1989).

5) A.M.Mackay. *Chemical Behavior of Morpholine in the Steam -Water Cycle of a Candu-PHW Nuclear Power Plant.* Proceedings 1991 Symposium on Chemistry in High Temperature Aqueous Solutions, EPRI TR-102706 (1993).

6) J.K. Lin and C.C. Lai, Anal. Chem.; **52**, 630 (1980).

7) H. Koizumi and Y. Suzuki, J. High Resolut. Chromatogr. Chromatogr. Commun.; **10,** 173 (1987).

8) C.Lamarre, R. Gilbert and A. Gendron. *Liquid Chromatographic Determination of Morpholine and its Thermal Breakdown Products in Steam-Water Cycles at Nuclear Power Plants.* J. Chromatography **467**, 249 (1989).

9) R.Gilbert and S.E.Saheb. *Field Measurements of the Distribution Coefficients of Chemical Additives used for Corrosion Control in Steam-Water Cycles.* Materials Performance **26**, 30 (1987).

10) R.Gilbert, C.Lamarre and Y.Dundar. *The Effects of Morpholine, Ammonia, and Hydrazine Treatment on Secondary System Chemistry in Candu Power Plants.* Proceedings of the 10th Annual Conference of Canadian Nuclear Society, vol.3, 17-1 (1989).

©11) R.Gilbert, Y.Dundar and A.Marchand. *AVT using morpholine alone: a unique experience at a Cand-PHW Plant in Canada.* NEA/CSNI-INIPEDE Specialist Meeting On Operating Experience With Steam Generators, Brussels, Belgium (1991).

12) D.S.Sparks. *Environmental Soil Chemistry.* Academic Press p 57, 1995.

13) J.F.Selmann, M.E.Rogers and E.C.Sanford. *Characterization vs. Identification of Organics in Boiler Feed Water Treatment*. International Water Conference 1986, paper 13.

14) A.M.Mackay. *The effect of morpholine, ammonia, and hydrazine treatment on secondary system chemistry in Candu Power Plants.* Proceedings of the Second International Steam Generator and Heat Exchanger Conference (Toronto, Canada), page 8.55 (1995).

15) R. Gilbert and C.Lamarre. *Field Investigations on Decomposition Products of Morpholine in the Secondary Cycles of CANDU-PHWR Plants.* Report of Institut de Recherche d'Hydro-Quebec. IREQ-4781, 1991.

TABLE I

Concentrations of amines (mg/dm^3) in the secondary system at Embalse NPP.

Sample	Date	Morpholine	Ammonia	EA	AEE	MA
FP	10/10/96	5.1	0.44	0.02	0.03	0.09
	28/03/95	6.3	0.60	0.10*		0.12
	29/03/95	7.9	0.51	0.16*		0.12
S	10/10/96	4.7	0.39	0.04	0.05	0.07
	28/03/95	6.6	0.36	0.14*		0.13
	29/03/95	9.4	0.53	0.20*		0.15
CSGB	10/10/96	4.1	0.15	0.20	0.04	0.04
	28/03/95	5.7	0.10	0.16*		0.05
	29/03/95	7.0	0.11	0.16*		0.06
MS	10/10/96	4.3	0.45	<0.01	0.08	0.08
	28/03/95	6.5	0.63	0.14*		0.13
	29/03/95	7.4	0.62	0.18*		0.13
CEP	10/10/96	4.8	0.55	0.02	0.03	0.09
	28/03/95	6.3	0.51	0.14*		0.12
	28/03/96	9.5	0.42	0.18*		0.16

EA: ethanolamine. AEE: 2(2-aminoethoxy) ethanol. MA: methylamine. CSGP: combined steam generator blowdown. S: main steam. MS: moisture separator. FP: feedwaterpumps. CEP: condenser extraction pumps.

(*) These values correspond to EA + AEE concentrations.

TABLE II

Concentrations of organic acids (μg/dm^3) in the secondary system at Embalse NPP.

Sample	Date	Formic	Acetic	Glycolic
FP	10/10/96	42	27	14
	28/03/95	23	5	5
	29/03/95	30	19	10
S	10/10/96	31	25	11
	28/03/95	20	5	7
	29/03/95	29	11	7
CSGB	10/10/96	43	44	22
	28/03/95	42	16	11
	29/03/95	32	8	6
MS	10/10/96	26	11	7
	28/03/95	22	8	7
	29/03/95	39	8	8
CEP	10/10/96	24	12	5
	28/03/95	20	7	7
	29/03/95	27	7	14
Makeup water	10/10/96	21	10	18
	27/01/97	13	3	5

TABLE III

Concentration of amines and organic acids in the steam generator blowdown of CANDU NPP

PRODUCT	CNE	G-2[a]	BRUCE A[b]	PICK. B[c]	DAR. A[d]
Morpholine (ppm)	4.1	4.79	5.5	2.8-3.5	-------
Ammonia (ppm)	0.06-0.17	0.011	0.4-0.5	0.12-0.19	1.4 - 1.6
Methylamine (ppb)	51-64	24	50	50	-------
Ethanolamine (ppb)	200	51	307-392	155-707	-------
AEE (ppb)	40	198	--------	--------	-------
Acetate (ppb)	8-15	15	302-338	15-204	62-129
Formate (ppb)	32-42	10	11-13	4-27	3
Glycolate (ppb)	6-11	69	67-68	9-152	12-15

a) Data from Ref. 10.
b) Data from Ref. 14 (Contamination with acetate (ca. 1 ppm), ethanolamine (0.2-0.5 ppm), glycolate (50 ppb) and formate (0.5 ppm) in additives injection tank).
c) Data from Ref. 14 (Contamination with ethanolamine (ca. 700 ppb) in morpholine injection tank).
d) Data from Ref. 14 (Contamination with formate (180 ppb), acetate (750 ppb) and glycolate (700 ppb) in additives injection tanks).

CNE : Embalse NPP; G-2: Gentilly-2 NPP; PICK.B: Pickering-B NPP; DAR.A: Darlington-A NPP; AEE: 2-(2- aminoethoxi) ethanol

TABLE IV

Distribution Coefficients of Morpholine and its Degradation Products in CANDU NPP

PRODUCT	K^{SG} CNE	K^{SG} G-2[a]	K^{SG} OTHERS[b]	K^{HP} CNE	K^{HP} G-2[a]	K^{HP} OTHERS[b]
Ammonia	2.6-4.8	3.64	1.4-4.3	0.6-0.9	0.8	0.7-1.2
Morpholine	1.1-1.3	1.10	0.9-1.4	1.0-1.3	0.87	1.0-1.5
Methylamine	1.8-2.6	2.33	-------	0.9-1.2	1.75	-------
Ethanolamine.	0.2	0.27	0.17-0.4	-------	0.17	-------
AEE	1.25	0.97	-------	1.25	1.22	-------
Glycolate	0.5-1.2	<0.03	0.02-0.3	0.9-1.6	<0.5	-------
Formate	0.5-0.9	<0.2	0.13-0.75	0.7-1.2	<0.33	0.5-0.6
Acetate	0.3-1.4	1.27	0.1-0.7	0.6-2.3	0.17	-------

a) Data from Ref. 10.
b) Data from Ref. 14 for Bruce A, Pickering B and Darlington A.

FIGURE 1: Schematic diagram of the Secondary Side of Embalse NPP showing the sampling points. (1) Moisture separator, (2) Main steam, (3) Combined steam genarator blowdown, (4) High pressure heater outlet, (5) Condensate pump discharge.

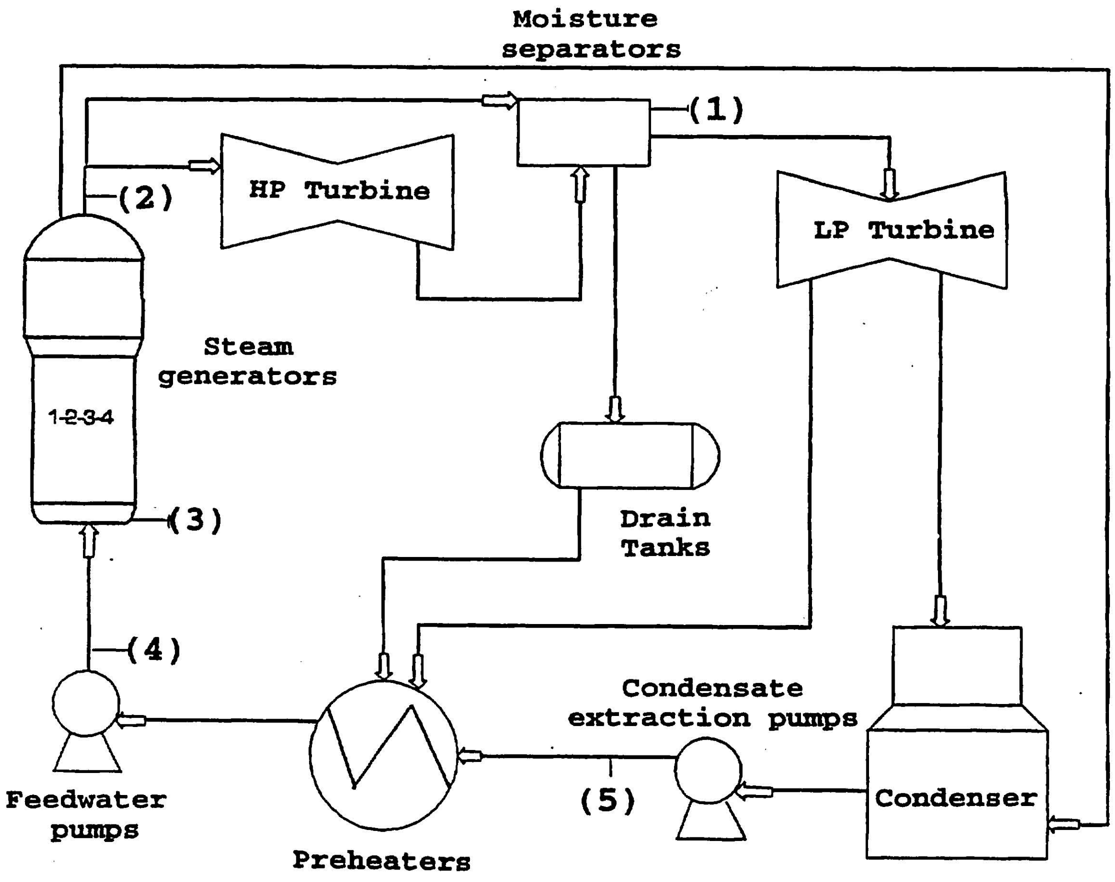

FIGURE 2: Reaction scheme for the thermal decomposition of morpholine according to Gilbert *et al.* (Ref.[11])