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M. Dekhil
SIAPE, Tunisia

RESUME

La protection de l'environnement est perçue dans le monde en général et en Tunisie en particulier de plus en plus comme une composante importante d'un développement global et durable répondant à l'aspiration des populations à une qualité de vie meilleure.

Cette perception s'est matérialisée en Tunisie dans le domaine de l'industrie de transformation des phosphates par un ensemble d'actions touchant aussi bien l'environnement dans les centres de production en Tunisie (traitement des principaux rejets : $SO_2 / SO_3 - NH_3$ - phosphogypse) que celui dans les pays clients (traitement des principales impuretés obtenues dans le phosphogypse (cadmium, P_2O_5)).

L'exposé traitera de l'ensemble de ces actions en faveur de l'environnement en détaillant les moyens mis en oeuvre pour identifier les solutions (étude d'impact, mise au point des procédés, etc.).



1. INTRODUCTION

The discovery in 1885 of a calcium phosphate deposit in the gorges of Thelja in the south-west Tunisia led to the development of the phosphate industry. Rock phosphate production increased from 178,500 t in 1900 to 6.5 million t at present. Tunisia ranks 5th in the world after the USA, Russia, Morocco and Jordan. The potential reserves are estimated at almost 600 million tons.

Mining and beneficiation operations are run by the Compagnie des Phosphates de Gafsa (GPS) which presently operates:

- 6 quarries
- 4 underground mines
- 5 beneficiation units

The processing activity is in the hands of the Groupe Chimique Tunisien (GCT) which includes SIAPE and SAEPA. This activity started in 1952 with the start-up of the TSP plant at Sfax. Since then, the processing industry kept on developing. To-day, it processes 5.5 million t phosphate rock (e.g. 85% of the national production) in four sites: Gabes, Skhira, Mdhilla and Sfax.

The fast development of the phosphate sectors raised the pollution problem generated by that industry.

This problem becomes increasing urgent owing the ever increasing pressure for environment protection and management in our modern societies. The universal awareness resulted in more stringent standards being imposed to the industry.

In Tunisia, a global environment strategy was decided. It enabled to establish, starting from a comprehensive inventory of pollution sources in the various activity centres, an action programme defining priorities in the field of environment protection on one side and reconciling the development requirements with the environment protection constraints on the other.

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The phosphate sector was given top priority. An environment programme was developed to control the negative effect of that sector.

The purpose of this paper is to present the part of the programme concerning the processing industry, from the preparation of the programme to its implementation. It is divided in three parts reflecting the approach followed to tackle the problem.

- The first part presents the various studies conducted on the impact of the discharges.

The discharges are investigated and compared to the emission standards to determine those for which environment impact studies are necessary. They enabled to identify the discharges to be controlled in first instance.

- The second part presents the solutions adopted for the treatment of the discharges for which the impact on environment was established.

For each pollutant, the method used to identify the solution is presented. The state of progress of achievement is then indicated.

- The third part presents the processes worked out by the Groupe Chimique Tunisien to control a few impurities contained in phosphoric acid.

2. IMPACT OF THE DISCHARGES

2.1. Production capacity of each site

	Gabes	Skhira	Mdhilla	Sfax	Observations
Sulphuric acid t/d	8,400*	3,500	1,500	1,050	*Six units
Acid 28% P ₂ O ₅ t/d P ₂ O ₅	2,210	1,100	480	420	
Acid 54% P ₂ O ₅ t/d P ₂ O ₅	2,410	1,200			
DAP t/d	2,400*	-			*Two units
TSP t/d	-	-	1,350	1,000	
Nitric acid t/d	780	-	-	-	
Nitrate 33.5% N t/d	1,000	-	-	-	

We notice that the Gabes site is characterized by:

- a high concentration of production units (50% of the phosphate is processed there)
- the variety of products obtained

2.2. Performances (in terms of wastes), of the processes used

Table 1 indicates the efficiency, in terms of wastes, of the processes used. These performances are compared with some standards. We notice that:

- the fluorine, NO_x and nitrate containing waste gases comply with the standard. Their impact on the environment is assumed to be negligible.
- the SO₂/SO₃ gaseous discharges exceed the standards.
- the ammonia waste gases must be treated for reasons to be explained later.
- fluorine, P₂O₅ and phosphogypsum discharges in the sea exceed the standards.

2.3. Wastes balance

From an environmental point of view, the Gabes site is characterized by:

- a large concentration of sulphuric acid units (6 units - 8400 t/d)
- ammonia discharges
- phosphogypsum discharges (11,000 t/d) onto the sea. In the other sites, phosphogypsum is stacked ashore.

The impact studies presented hereunder were accordingly conducted for the discharges of this site. The results are valid for the other sites.

2.4. Impact studies of SO₂/SO₃ gaseous discharges

The impact was determined on the basis of SO₂/SO₃ ambient air concentration at the ground level due to these discharges. These concentrations are compared to the limit values set by the standards for the protection of human health and environment.

The limit values adopted were those of the EEC standard, namely:

- value 50% of the 24 h means for one year: 80 µg/m³
- value 98% of the 24 h means for one year: 250 µg/m³

The annual arithmetic mean, very much in use for the environment, will also be checked. The US standard sets the limit at 80 µg/m³ average.

Failing systematic measurements of pollutants in the atmosphere pollutant concentrations at the ground level were quantified by numerical simulation. The statistical model SIMPOL of EdF was used. A brief presentation of this model is included in Appendix I.

In that model, the physics of dispersion of the pollutant is simplified to enable the use of a quick analytical formulation which can simulate long development. This formulation, however, is approved and used with some variations in many countries. In the USA, the models approved by EPA (Environmental Protection Agency) are of that type. In France, these models are recommended by the Atomic Energy Board following the guidelines of International Agency for Atomic Energy.

If the meteorological sequences are good and the emissions well described, these models give satisfactory results, and, hence, quite suitable for the industrial unit study and design stages.

The results of simulations are given under the unfavourable assumption that no reaction impoverishes the plumes (See 2.5. in which 25% of SO₂ and 100% of SO₃ are neutralized by ammonia in the atmosphere).

a. Annual arithmetic mean

The land is normally more affected by pollution than the sea (predominance of winds from the sea): maximum value of annual mean on the land.

The area where concentrations exceed the USA standard covers about 9 km² west of the site between Bouchemma and Ghannouch (sector 13 from 0 to 4 km and sector 14 from 0 to 6 km).

b. Value 50% of 24 h means in one year

The area where the EEC standard is exceeded is sector 14, from 0 to 4 km and sector 13, from 0 to 2 km. One can notice that this standard is less stringent than the arithmetic mean.

c. Value 98% of 24 h means in one year

The area where the EEC standard is exceeded is divided into two parts, one above the sea (the most extensive) and the other on the land including the north west part of Gabes and the cities of Bouchemma, Ghannouch, Chenini and Aouinet.

Table 2 gives the results of simulations for some studied spots. Figure 1 indicates the calculation grid, the location of these spots.

2.5. Study of the impact of gaseous ammonia discharges

For ambient air, there is not legal limit for ammonia concentration. France set for the gas indicative exposure limit value (VLE) and the average exposure limit values (VME) acceptable in the atmosphere of work rooms. These values correspond to the respective concentrations of 36 mg/m³ (50 ppm) and 18 mg/m³ (25 ppm).

It should be noted that the maximum concentrations acceptable in the work environment are 5 to 30 times higher, on the average, than the limit concentrations accepted in the outside atmosphere for the same pollutants.

The average concentration accepted in the ambient air would then be 600 µg/m³.

The simulations carried out on that gas showed that:

- the annual average does not exceed 39 µg/m³
- the average threshold does not exceed 250 µg/m³

Actually, the impact of ammonia, the only alkaline compound discharged, results from the fact that in the atmosphere it reacts with other wastes (especially SO₂/SO₃) to produce mist. To evaluate this phenomenon, the visibility parameter was adopted.

The visibility was estimated by using Koschmieder formula on the hourly ammonium sulphate aerosol concentrations produced by the reaction between SO₂/SO₃ and ammonia (see method of calculation in Appendix 2).

The model used assumes that the NH₃ and SO_x plumes are closely mixed whatever the climatic conditions. This assumption probably results in an overestimate of the reduction of visibility. Consequently, the results should be considered as relative values.

Table 2 gives, for the localities under study, the number of hours per annum (in relative value) of visibility lower than or equal to 500 m (light mist).

2.6. Study of the impact of sea discharges

All the studies done in the Gulf of Gabes show:

- A significant important reduction of the posidonia acreage

This regression is actually noticed all over the Mediterranean. The origin of the phenomenon is probably multiple. The eutrophication of the environment, whether recent (urban and industrial wastes) or more ancient (picking of sponges with "gangaves", shallow trawling), seems to be superposed to more profound disequilibria (sedimentary cycles).

- A decrease in seafood resources

This decrease results from the destructive impact of illegal deep trawling, an increasingly intensive and localized fishing, an uncontrolled chemical pollution detrimental to the reconstitution of fish population and the regression of the posidonia acreage.

To estimate the part of the discharges from the Groupe Chimique Tunisien in that process, several rounds of sampling and analysis of sea water were organized in the Gulf. They gave the following results:

- Temperature of sea-water:
At the beach level, a rise of temperature was noticed. It is localized and no longer noticeable 50 m away.
- Turbidity and coloration:
Suspended materials considerably reduce the penetration of light, with negative effects on aquatic life. Near the beach, the sea-water is always blackish (organic matter). The situation improves 1200 m away.
- Fluorine: the situation can be summarized as follows:
In all directions, the recordings indicate, at the surface as well as in depth, free fluorine contents under 10 mg/l (a value considered as an acceptable limit for fauna and flora).
Outside a zone located south of the discharges, the concentrations are less than 3 mg/l.
The change in the present phosphogypsum disposal system will result in a lower fluorine impact. Indeed 54% of the amount of fluorine presently discharged will be eliminated. The limited impact of this pollutant will become negligible.
- Phosphate (PO_4): the situation can be summarized as follows:
In all directions, the recordings indicate, at the surface as well as in depth, the free PO_4 contents lower than 4 mg/l
Outside a zone located south of the discharges, the concentrations are less than 2 mg/l.
The change in the present phosphogypsum disposal system will result in a lower phosphate impact. Indeed, 91% of the amount of phosphate presently discharged will be eliminated. The impact of that pollutant will then become negligible.
- Heavy metals:
Experimental investigations confirmed a cadmium contamination of certain areas.
More generally, the impact on the marine environment of the discharges from the Groupe Chimique can be summarized as follows:
 - The flora and the fauna completely disappeared in a 3 km² area around the discharge point.
 - 4.5 km from the coast, the flora seems healthy but the fauna is not very developed.
 - The situation is again normal 8 km away from the coast

3. WASTE TREATMENT

3.1. Sulphurous gases

3.1.1. Identification of the solutions to be considered

The search for solutions to minimize the impact of these wastes followed two main routes:

- a. Better dispersion of the wastes in the atmosphere with higher stacks
- b. Reduction of the emissions:

Two methods were investigated to reduce emissions:

b.1. SO₂/SO₃ gas scrubbing with ammonia

Although the percent reduction of the SO₂/SO₃ is of the same order of magnitude as that obtained with the double absorption process, this method was rejected for the following reasons:

- The product obtained (34 t/d 100% sulphate for each sulphuric acid unit of 1500 t/d converted) has no commercial outlet.
- The use of this production in solid form in the two DAP units can only be partial owing to the role played by sulphuric acid in gas scrubbing.
- At the technical level, ammonia scrubbing is difficult to manage and can be a source of pollution in case of trouble in the operation parameters or in case of problems in the demister (white sulphate fumes in the stack).
- The investment in the case of solid sulphate production is identical to that of double absorption. It is lower in the case of the production of 40% sulphate solution to be used in DAP units instead of sulphuric acid. However, that possibility requires the use of a higher proportion of concentrated acid, the need of a continuous operation of DAP units which require a pre-neutralizer.

b.2. Transformation of the units to double absorption

This method was used to reduce emissions.

This transformation is based on the modification of converters by the elimination of air injections after the 2nd and 3rd catalyst layers on the one hand and the inclusion of an airtight plate between the 3rd and 4th catalyst layers on the other.

The partially converted gas leaving the 2nd catalytical level is cooled in a hot exchanger by heat exchange with the gas coming from the interabsorption and returning to the 3rd catalyst layer.

After leaving the 3rd layer, the gas is sent to the new interabsorption tower, through a gas/cold gas exchanger and an economizer on the boiler water. After absorption of SO₃ formed when passing the first three conversion layers, the gas is returned to the 4th layer through gas/cold and hot gas exchangers.

No change in the gas loop after leaving the first catalyst layer: economizer, final (existing) absorption tower and stack.

This method enables to reduce by more than 80% the SO₂/SO₃ discharges.

3.1.2. Solution adopted

Various combinations of the two possible options were studied. The results of these simulation studies show that:

- the conversion of two units to double absorption :
 - does not enable to comply with the annual standard. The standard is exceeded in an area of about 6 km² west of the site between Bouchemma and Ghannouch (sectors 13 and 15 - zone 0-4 km).

- . does not enable to comply with the standard concerning the frequency of exceeding the threshold of $250 \mu\text{g}/\text{m}^3$. The localities of Bouchemma and Ghannouch, among others, are concerned.
- The conversion of four units to double absorption:
 - . enables to comply with the annual standard. Note that sector 14, zone 0-2 km is at the limit ($78 \mu\text{g}/\text{m}^3$).
 - . does not allow to comply with the standard concerning the frequency of exceeding the threshold of $250 \mu\text{g}/\text{m}^3$: sector 4, zone 0-6 km, sector 5, zone 2-4 km, sectors 13 and 14, zone 0-4 km.
- The conversion of four units to double absorption and raising the stacks of the two other units to 70 m:
 - . enables to comply with the annual standard with a good safety margin ($38 \mu\text{g}/\text{m}^3$ maxi)
 - . enables to follow the threshold of $250 \mu\text{g}/\text{m}^3$ with a good safety margin.

This solution was adopted and implemented.

Table 2 gives the results obtained in the localities studied.

Note that, when the programme is completed, the SO_2 emissions in the Gabes site will come down from 109 t/d to 43 t/d SO_2 , e.g. to the level of the Skhira site. It is concluded that, for the other sites, the quality standards will be met.

3.1.3. Implementation of the solution adopted

- a. 70 m high stack: the two existing stacks, respectively 35 and 50 m high were replaced by a unique 70 m stack. The new stack started operating in November 1993.
- b. Conversion of the four units to double absorption

This project is being implemented:

- the first converted unit started operating in March 1994
- the three others will start operating in July, August and September 1994, respectively.

The converted unit gave the following results:

- SO_2 emission : 1.275 kg/t H_2SO_4
- SO_3 emission : 0.028 kg/t H_2SO_4
- Acid mist : 0.02 kg/t H_2SO_4

3.2. Gaseous ammonia

The emission abatement was obtained:

- For the first unit: by the addition of a Venturi in the gas tube before the gas scrubbing tower of the granulation section on the one hand and by the addition of a second scrubbing stage for the gases using sulphuric acid on the other.
- For the second unit: by the addition of a second scrubbing stage with sea water for the gases of the granulation section. The replacement of sea water by sulphuric acid will take place later.

These modifications, completed in May and July 1993, enabled to reduce by 80% the ammonia emissions to the atmosphere. Table 2 shows the impact of these modifications for the localities studies.

The results are confirmed in actual facts. Mist almost disappeared in the region.

3.3. Phosphogypsum disposal in the sea

An overall study including technical and economic environmental aspects for an optimum solution of this problem was ordered.

The first stage of this study is completed. It enables the estimate of all the possible options to monitor the phosphogypsum.

These options include:

- Keeping the present system of sea disposal
- Discharge in the open sea using a submerged pipe fitted with spray nozzles, or barges
- The reuse and recycling, with possible changes in the process to facilitate the recycling
- The closure or transfer of the phosphate processing activities
- The return of phosphogypsum to the mine
- The inland disposal using a humid or dry discharge

The analysis led to the conclusion that the only viable option from environmental, technical and economic points of view would be land disposal.

The search of potential sites for inland disposal was done by assessing, in a first stage, technical and environmental localization criteria. In a second stage, the identification of potential sites was carried out on a total of 12 sites.

To evaluate these sites, a comparison matrix of various criteria and of their respective importance was established.

The analysis of results enabled to preselect a site located 20 km north west of the factories for a more comprehensive study. A tender is under preparation to achieve the following activities on the site:

- Photogrammetry and topometry
- Measurements and geotechnical and hydrogeological analysis
- Hydrology
- Vegetation
- Ground fauna and birds

3.4. Other measures in favour of the environment: use of humid phosphate

Within the policy of energy saving of reduction of costs and environment protection (dust), a project was worked out to carry out the necessary modifications to feed the factories in the centre of Gabes with filtered phosphate (12-15% water) instead of dry phosphate (1.5% water).

The dry phosphate is stored in 6 cylindrical bins made of prestressed concrete varying from 14 to 20 m diameter and 17 to 28 m height.

Two alternatives were studied for the storage of humid phosphate:

- the use of existing bins. This solution is a novelty in that field since there is no reference to it in the world.
- the establishment of storage areas with scraper reclamation. The investment involved in this option is twice the first one.

It was then decided to assess the reliability of the "bin" solution, to modify one bin as a test. The modifications consisted in:

- applying a lining with a low rubbing rate
- installing a rotating paddle extractor in the bin
- putting in a diametral opening at the bottom of the bin
- installing air ventilators to promote the flowing of the product in case of plugging.

The bin was successfully put in operation in February 1993.

This solution is being extended to the five other bins. Gabes platform will be fully supplied with filtered phosphate by the end of 1994.

Various improvements on the feeding systems of the bins are also considered:

- Adaptation of the waggon dipping stations (angle of repose, lining with an anti-plugging material)
- Improvement of the storage feed systems (modification of the jetty points for the carriers, installation of screens)
- Installation of temporary circuits to feed the units during the modification operations.

4. TREATMENT OF SOME IMPURITIES CONTAINED IN PHOSPHORIC ACID

4.1. Regulations concerning impurities contained in phosphoric acid

The maximum impurity content is set as follows by some regulations:

	Dicalcium Phosphate (DCP)		Cadmium in fertilizers in mg Cd/kg P	Observations
	Cadmium in mg/kg	Fluor in mg/kg (ppm)		
Austria			120	Till 1/7/95
Denmark			200	
Finland			50	
Norway/Sweden			100	
Switzerland			50	
Belgium/Germany			205	Voluntary agreement
EEC	10 ⁽¹⁾	2000 ⁽¹⁾		(1) Content based on a 12% moisture (1) Correspond to a concentrated phosphoric acid containing: - 12.6 ppm Cd, - 0.25% F

4.2. SIAPE process for the treatment of impurities in the acid

Tunisian phosphate contains an average of 40 ppm Cd and 3.3% F. The DCP produced from that rock contains 36 ppm Cd and 0.3% F.

To comply with the new regulations, SIAPE developed and patented a process to reduce cadmium and fluorine contents of phosphoric acid. This process is based on:

- The use of phosphoric acid rich in solid material (up to 3%), containing 26 to 56% P_2O_5 and a temperature between 30 and 80°C.
- The use of an appropriate reagent. This reagent is injected under pressure co-currently with phosphoric acid in one or several columns. The reaction between the reagent and heavy metals is instantaneous.
- The separation by filtration, centrifugation or settling of the heavy metal complexes formed.

The phosphoric acid obtained after treatment contains 1 to 15 ppm Cd and 0.18 to 0.25% F.

An industrial plant of 230,000 t/yr P_2O_5 capacity was built in 1991 by the research services of SIAPE at Gabes with that process.

5. CONCLUSION

The achievement of the environmental programme presented in that paper will cost the national community almost 150 million dollars of which 40 are already committed for the treatment of gaseous wastes. In the difficult situation of the fertilizer industry, these actions show the real political willingness to counteract the effects of pollution produced by that sector.

No doubt that, when the programme is completed, Gabes will gradually recover its investments, namely:

- Tourism: Gabes has the only maritime oasis in the Maghreb
- Fishing: The Gulf of Gabes is the most productive fishing area in Tunisia, possibly one of the most important in the Mediterranean

TABLE 1: EFFICIENCY IN TERMS OF DISCHARGES OF THE PROCESSES USED

	EMISSIONS			STD	STANDARD REFERENCE
	Unit	Process	Quantity		
1. GASEOUS DISCHARGES					
SO ₂	Sulphuric	Simple contact	13 kg/t acid	2 to 2.6	USA-FRANCE
SO ₃		Simple absorpt.	1.7 kg/t acid		
NH ₃	DAP	TVA	3300 mg/m ³	-	
FLUORINE	Acid 28%	SIAPE	7 mg/m ³	10	FRANCE Law of March 1993
NOx	Nitric acid	Double pression	0.8 kg/t acid	1.5	USA
NITRATE	Nitrate	Prilling	100 µg/m ³		
2. DISCHARGES IN THE SEA					
FLUORINE in fluorinated waters	Acid 28%	SIAPÉ	425 mg/l	5	Tunisian standard TS 106.002
	Acid 54%	Evaporation under vacuum	318 mg/l		
PO ₄ in fluorinated waters	Acid 28%	SIAPE	Traces	0.18	
	Acid 54%	Evaporation under vacuum	56 mg/l		
GYPSUM	Acid 28%				
- MES			250 g/l	0.03	
- PO ₄			3200 mg/l	0.18	
- Fluorine			3000 mg/l	5	
- Cadmium			2.9 mg/l	0.005	

TABLE 2: RESULTS OF NUMERICAL SIMULATIONS

	Initial situation			Situation after modification		
	(1)	(2)	(3)	(1)	(2)	(4)
CHATT ESSALAM	15	1	27	3	< 0.1	59
BOUCHEMMA	78	<u>94</u>	98	22	0.1	66
GHANNOUCH	79	<u>77</u>	100	15	0.1	76
GABES	24	<u>20</u>	27	6	< 0.1	70
CHENINI	48	<u>46</u>	67	13	< 0.1	80
TEBOULBOU	15	3	19	4	< 0.1	94
METOUIA	40	7	54	11	< 0.1	95
AQUINET	48	<u>30</u>	70	11	< 0.1	82
OUDHREF	33	5	41	9	< 0.1	96

(1) Annual arithmetical mean in µg/m³ (Norm: 80 µg/m³)(2) Frequency in % in an excess of the threshold of 250 µg/m³ (norm: 20%)

(3) Number of hours per annum (relative value) of visibility lower than or equal to 500 m (light mist)

(4) Percentage of visibility improvement

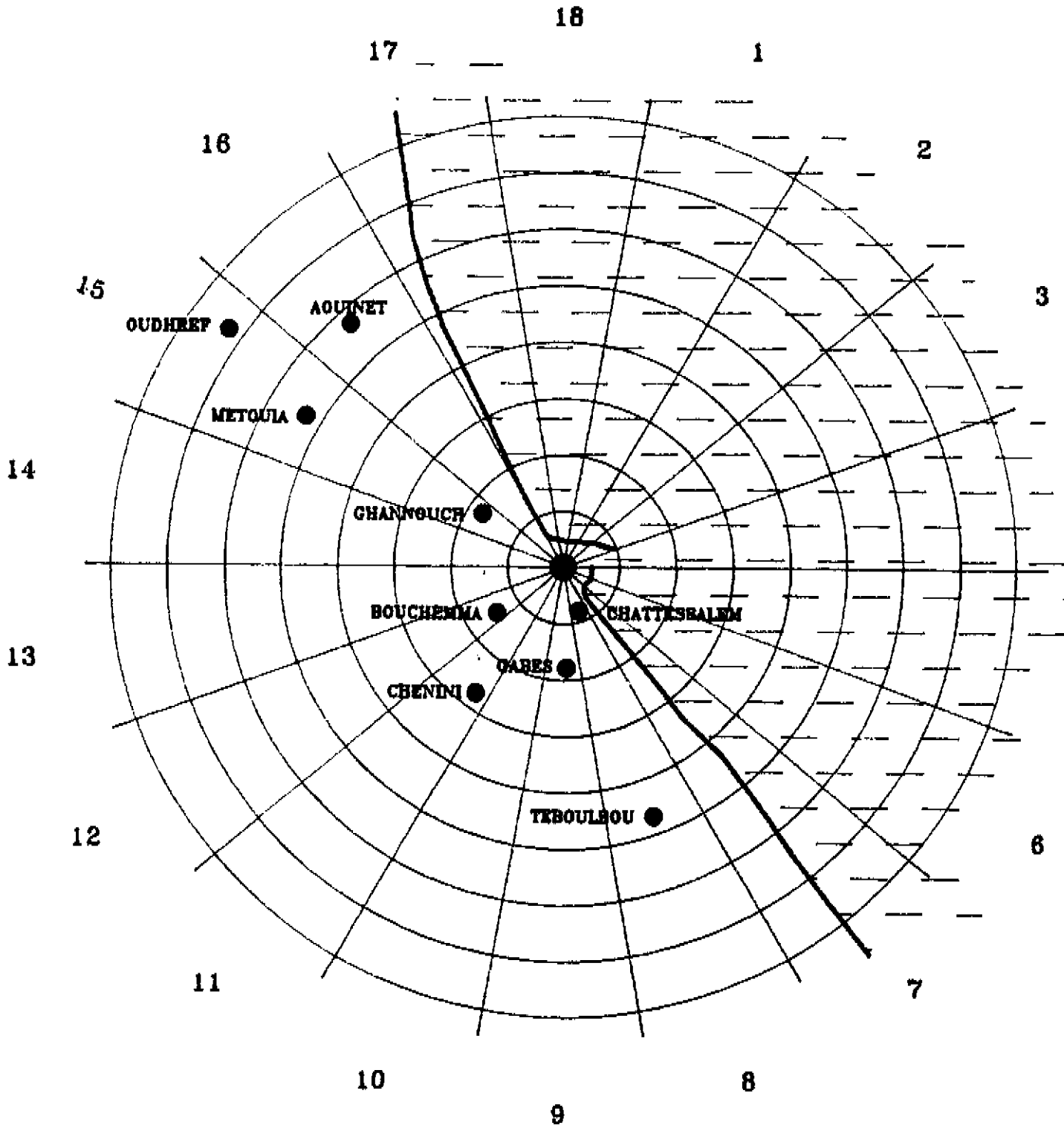


FIGURE 1: POSITION OF THE LOCALITIES STUDIED

APPENDIX 1

**MODELIZATION OF THE ATMOSPHERE DISPERSION OF POLLUTANTS
PRESENTATION OF THE STATISTICAL MODEL (SIMPOL)**

1. GENERALITIES

On the basis of hourly meteorological data collected on the site, a simulation of the emissions, of the plumes and of the resulting ground pollution in the field of calculation is carried out.

The meteorological data considered are the hourly measurements of wind (module and direction), nebulosity and ground temperature for a five year period of measurements (1985-1989).

The simulated phenomena are:

- the upraising of the plume as a result of its own dynamics
- the pollution transportation by the wind
- the diffusion of the plume according to the turbulent state of the atmosphere

2. METHOD OF CALCULATION

For each hourly measurement, we estimate:

a. The stability of the atmosphere at that instant:

For lack of direct measurements of turbulence (SODAR measurements for example), the atmospheric stability was estimated by an indicator: Pasquill class. The atmospheric stability is then classified in 6 categories:

- 1. Class A: very strongly unstable
- 2. Class B: very unstable
- 3. Class C: unstable
- 4. Class D: neutral
- 5. Class E: stable
- 6. Class F: very stable

Turbulence has two origins, one mechanical, the other thermal.

The mechanical turbulence is predominant in strong wind and tends to make the atmosphere thermally neutral. The mechanical effects are determined by an indicator I using the measure V11 in m/sec of the wind speed at 11 m.

V11	0 to 0.5	0.5 to 1.5	1.5 to 3.5	3.5 to 5.5	5.5 to 6.5	> 6.5
I	1	2	3	4	5	6

Thermal turbulence results in strong instabilities when the ground is overheated and when the wind lets the natural convection established itself.

The thermal effects are determined on the basis of a radiance indicator R using the height of the sun H (which varies with the day of the year and the hour of the day), as well as nebulosity N.

	night	$0 \leq H < 15^\circ$	$15^\circ \leq H < 35^\circ$	$35^\circ \leq H < 60^\circ$	$60^\circ \leq H \leq 90^\circ$
N = 0	R = 5	R = 5	R = 3	R = 2	R = 1
N = 1	R = 5	R = 5	R = 3	R = 2	R = 1
N = 2	R = 5	R = 5	R = 3	R = 2	R = 1
N = 3	R = 5	R = 5	R = 3	R = 2	R = 1
N = 4	R = 5	R = 4	R = 6	R = 2	R = 1
N = 5	R = 4	R = 4	R = 6	R = 3	R = 2
N = 6	R = 4	R = 4	R = 6	R = 3	R = 2
N = 7	R = 4	R = 4	R = 6	R = 3	R = 2
N = 8	R = 6	R = 6	R = 6	R = 6	R = 3

Class Pasquill is determined by crossing the two indicators I and R according to the following Table:

	R = 1	R = 2	R = 3	R = 4	R = 5	R = 6
I = 1	A	A	B	F	F	D
I = 2	A	B	B	E	F	D
I = 3	A	B	C	E	F	D
I = 4	B	C	C	D	E	D
I = 5	C	C	D	D	D	D
I = 6	C	D	D	D	D	D

The principles already presented appear again in that procedure:

- (1) in strong wind, the atmosphere is well stirred and neutral (D),
- (2) in mild wind and if thermal energy is available close to the ground, natural convection can be established (A, B, C)
- (3) failing that, the atmosphere is stable (E, F)

b. The wind speed (U) at the level of the stack

The effects of rubbing the round result in the development of an atmospheric limit layer, the characteristics of which are usually expressed in a power law.

$$U = V_{11} \times \left[\frac{H p}{11} \right]$$

with H = height of the stack

p = 0.25 for classes A, B, C and D

p = 0.5 for classes E and F

The profile is the more uniform (p → 0) that the flow is turbulent. It tends towards a parabolic profile for a laminar flow.

This extrapolation is made for each stack. The wind is important since it modifies:

- the final height of the plume (the calculation of the overheight depends on it)
- the speed of transpiration-diffusion of effluents

c. Plume of heightened stack

By the effect of its own kinetics and thermal energy, the plume can go up substantially. In the search, for a quick estimate, the intermediate stage between the stack exit and the stage of transportation-diffusion, where the thermodynamic characteristics of the plume and the ambient air merged is not taken into account. In the simulation, the actual source R is replaced by a virtual and punctual source S'. The horizontal distance between S and S' is negligible in relation to the distance of S or S' to the point of calculation.

The overheight formulae for sources where flotability phenomena predominate depend on wind U, the difference in temperature and stability.

Briggs formula (1972):

- . For good diffusion classes A, B, C, D

$$\Delta H = 38.71 \frac{\left\{ gwD^2 \frac{T_s - T_a}{4T_s} \right\}^{3/5}}{U}$$

ΔH : overheight of the plume

g: 9.81 m/s²

w: gas exist velocity

D: diameter of the stack

T_s: gas temperature at the exit of the stack in °K

T_a: air temperature in °K

For classes E and F, the plume is hampered:

$$\Delta H = 2.6 \frac{\left\{ gwD^2 \frac{T_s - T_a}{4T_s} \right\}^{1/3}}{\{ sU \}^{1/3}}$$

with s: stability parameter defined as follows:

$$s = \frac{g \frac{\partial \theta}{\partial z}}{T_a}$$

where $\frac{\partial \theta}{\partial z} = 0.02$ °K/m in class E and 0.035 °K/m in class F

An additional assumption that there is no interaction of the plumes of stacks in the different sectors is made. Strictly speaking, the combination of plumes could increase somewhat the overheight of the resulting plume and the fact that this phenomenon is not taken into consideration leads to overestimate of the concentration (raising character).

d. Mean concentrations in 10 minutes

On the basis of the assumptions considered in that study, the solution of the equation of pollutant transportation-diffusion in the atmosphere can read:

$$C = \frac{Q}{\pi \sigma_y \sigma_z U} e^{-0.5 \left[\frac{d}{\sigma_y} \right]^2} e^{-0.5 \left[\frac{H + \Delta H}{\sigma_z} \right]^2}$$

Q: pollutant flowrate

d: horizontal distance of the calculation point in relation to the axis of the plume

H: stack height

σ_y and σ_z : standard-deviations

The standard deviations are derived from experience. They depend on the stability of the atmosphere since they represent its diffusion characteristic and are related to the distance from the source. The most commonly used laws, failing values for the site, are those by Pasquill-Gifford.

e. Mean concentrations in one hour

These laws were established on tracing experiments taking sampling times of 10 min. It is necessary to calculate mean hourly concentrations since climatic data are available and elementary calculations are made over hourly periods.

Indeed one notices that the longer the sampling period, the smoother the mean concentrations in a given point (cutting off of the highest concentrations): natural wind variations cause an additional dispersion of the pollutant.

Passage coefficients are 0.7 for all stability classes.

3. IMPLEMENTATION OF THE MODEL

In order to optimize the time of calculation, a classification of the climatic conditions is worked in:

- 6 classes of speed
- 18 classes of direction
- 6 classes of stability

A climatic situation thus corresponds to one of the 648 typical predefined situations.

The calculation grid is a polar grid made of 18 sectors 20° each including 10 paving stones. A paving stone is then a sector of 20° opening and 2 km length.

The mean concentration of a paving stone is obtained by establishing the average of 10 points distributed equally in that stone.

Still winds are not dealt with. They are considered by the code of missing values. If, during the day, more than 50% of the measurements are present, the value of these measurements will give the daily average. On the other hand, daily mean concentrations will be invalidated for that day. Please note that still winds only represent 4.6% of cases.

APPENDIX 2

IMPACT OF ATMOSPHERIC DISCHARGES ON THE REDUCTION OF VISIBILITY
METHOD OF CALCULATING VISIBILITY**1. VISIBILITY REDUCTION PARAMETER**

The distance at which an observer can spot an ideally black object standing out against the sky on the horizon is related to a coefficient b called extinction coefficient (Koschmieder relation).

Considering that a contrast level of 0.02 is the lower limit discernible by human eye, the distance of vision (or visibility) is:

$$\text{Visibility} = \frac{-\text{Lg } 0.02}{b} = \frac{3.912}{b}$$

The predominant factor in the extinction b is the diffusion of light by particles (scattering).

It was, indeed, shown experimentally that the reduction of visibility due to the pollution of large industrial towns was largely due to the phenomenon of diffusion of light by particles forming aerosols of a small size, active in a fairly narrow particle range (0.2 to 1.5 μ) and that ammonium sulphate, among the particulate species present, was alone responsible for more than 2/3 of the diffusion coefficient measured.

Visibility is in direct relation with the content C of sulphate in aerosol.

$$\text{Visibility (m)} = \frac{0.3991}{C}$$

2. INTERACTION BETWEEN POLLUTANTS PROMOTING THE FORMATION OF AEROSOLS

The relative proximity of emission sources of the industrial site, when climatic conditions are suitable, promotes contacts between the various substances contained in the discharges, generating chemical interactions.

Considering the reactivity of the various substances discharged on the one hand and the amounts issued on the other, a global outline, summarizing in an ideal case the thorough mixing of all the emissions of the site, was established.

The reactions promoting the formation of aerosols take place largely between ammonia and sulphur oxides:

- NH_3 reacts very quickly with SO_3 to form an aerosol of ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ of low particle size. The ammonium sulphate aerosol becomes hydrated in contact with the atmosphere and reaches a mean diameter of about 0.5 μ .
- Sulphur dioxide is converted into sulphate at the average rate of 4% per hour which, as soon as it is formed, reacts with excess NH_3 to give again ammonium sulphate.
- Free NH_3 , very soluble in water, is captured by ammonium sulphate hydrated aerosols and renders the latter alkaline.

- The aerosols then neutralize a fraction of ambient SO_2 , to the level of the amount of ammonia retained by them. As a result, the aerosols become larger by about 45% in diameter.

The influence of the other substances on the mass balance of aerosol formation remains modest: gaseous fluorides emitted are soon neutralized by NH_3 producing silicofluoride and particulate ammonium fluoride: $(\text{NH}_4)_2\text{SiF}_6$ and NH_4F . Although it has little impact on the overall mass balance, this neutralization is important, since it reduces the fluorides emitted against the plants especially.

Fluorides are less phytotoxic than H_2SiF_6 or HF , especially when the latter is associated with SO_2 .

In view of the limited amounts of NO_2 emitted, the formation of ammonium nitrate is negligible.

Overall, the hourly output of the main compounds resulting from the chemical interaction process would be as follows:

Excess SO_2	: 55,702 moles/h
$(\text{NH}_4)_2\text{SO}_4$: 17,370 moles/h

for discharges of 74,402 moles/h of SO_2 , 6,900 moles/h of SO_3 and 35,300 moles/h of NH_3 .

This estimate does not allow for chemical interaction phenomena between gaseous substances emitted by the different plants of the site, and does not consider the possible (and probable) combinations with the other atmospheric substances present of various origins such as gaseous or particulate pollutants of anthropogenic (road traffic, marine aerosols) origin.

3. EVALUATION OF THE CONCENTRATION OF THE AEROSOLS FORMED

It was found that the aerosol produced by the interactions is made almost exclusively of ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ and that almost all the NH_3 is involved in that reaction.

It is thus possible to establish an estimate of the aerosol contents by transposing the results of NH_3 concentrations obtained by modelling in the areas where sulphur oxides and ammonia are likely to be present.

When the molar concentrations are such that $[\text{SOx}] > 2 [\text{NH}_3]$, the mass concentration of dry $(\text{NH}_4)_2\text{SO}_4$ is:

$$132 \times \frac{[\text{NH}_3]}{17 \times 2}$$

namely:

$$[(\text{NH}_4)_2\text{SO}_4] \text{ in } \mu\text{g}/\text{m}^3 = 3.88 \times [\text{NH}_3] \text{ in } \mu\text{g}/\text{m}^3$$