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EDITORIAL

Upon special request of many of our Brazilian readers, we are publishing two articles in Portuguese dealing with the oil industry , "Presence of Mercury in Petroleum" and "Mercury Corrosion of Cryogenic Heat Exchangers".

This issue of the Journal also contains articles in English entitled "Chemical Characterization of Atmospheric Particles in Urban Areas of Rio Grande do Sul, Brazil" and "Glimpses of the History of Chemistry in Mexico".

The article on some aspects of the development of Chemistry in Mexico is in honor of some of our Mexican friends, readers and collaborators.

Lavinel G. Ionescu, A.A., B.S., M.S., Ph.D.
Editor

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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CHEMICAL CHARACTERIZATION OF ATMOSPHERIC PARTICLES IN URBAN AREAS OF RIO GRANDE DO SUL, BRAZIL – PRELIMINARY STUDY

E. C. Teixeira[1], C.F. Braga[1], J. Fachel[2], D. Migliavacca[1], J.D. Sanchez[3] , M.L.L.Fomoso[4]

[1] Fundação Estadual de Proteção Ambiental, Porto Alegre, RS, Brasil
[2] Departamento de Estatística, Universidade Federal do Rio Grande do Sul
Porto Alegre, RS, Brasil
[3] Fundação de Ciência e Tecnologia, Porto Alegre, RS, Brasil
[4] Centro de Pesquisa Geoquímica e Petrologia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brasil

ABSTRACT

This work reports the determination of the concentration and chemical composition of atmospheric particles in the urban districts of Charqueadas and Sapucaia do Sul, State of Rio Grande do Sul, Brazil. Chemical composition, morphology and particle size were analyzed using a scanning electron microscope with energy dispersive x-ray microanalysis (SEM-EDS).Cluster analysis showed that there were six types of particles: Fe-Zn, Fe, Si-Al, Si, Ca-S and Na. Factorial analysis from cluster data showed that particles rich in Fe-Zn, Si-Al and Ca-S appeared more frequently, indicating anthropogenic influence (vehicles, steel plant, coal fired power station).The experimental results and consideration of the wind directions show that the main source of pollution in Charqueadas appears to be due to coal mining and steel industries, while in Sapucaia do Sul due to steel plants and vehicles.

RESUMO

Este trabalho trata da determinação da concentração e composição química de partículas atmosféricas nos distritos urbanos de Charqueadas e Sapucaia do Sul, Estado do Rio Grande do Sul,Brasil. A composição química, morfologia e tamanho das partículas foram analisados usando um microscópio eletrônico de varredura acoplado com microanálise com energia dispersiva de raios-x (MEV-MED). Análise de enxames mostrou a existência de seis tipos de partículas: Fe-Zn, Fe, Si-Al, Si, Ca-S e Na.Análise fatorial indicou que partículas ricas em Fé-Zn, Si-Al e Ca-S eram mais frequentes, indicando influência antropogênica (veículos, indústria siderúrgica e usina termoelétrica).Análise dos resultados experimentais, junto com a consideração da direção dos ventos indica que as fontes principais de poluição em Charqueadas são a mineração do carvão e a indústria do aço, enquanto em Sapucaia do Sul são as siderúrgicas e o transito de veículos.

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INTRODUCTION

Anthropogenic sources may discharge fine particles of heterogeneous chemical composition into the atmosphere. These particles can cause a severe impact on human health due to the presence of organic and inorganic pollutants that may be deposited in the human respiratory system.

The type of particles present in the atmosphere originating from stationary emissions and mobile sources varies from country to country. These particles present heterogeneous characteristics, the larger ones usually originating from soil and the finer ones from emissions of anthropogenic sources.

Particulate concentration, regulated in most countries by environmental legislation is a pollution indicator but it does not specify chemical composition. Knowledge of the chemical composition of aerosols allows in many cases the identification of the source of pollution that may be anthropogenic .Many studies have been done in the past that identified chemicals species in atmospheric particles in urban and non-urban areas.[1]

The many techniques used to determine particle composition however failed to determine the speciation and distribution of elements in the aerosols.

Scanning electron microscopy with energy-dispersive x-ray microanalysis (SEM-SED)and particle induced x-ray emission (PIXE) have been used for particle characterization .[2-6] The results of these studies have permitted the determination of the size and type of particles as well as the relation of these characteristics to anthropogenic sources,

In Southern Brazil, particulate matter has been an issue of concern, specially due to the low efficiency of emission control systems for fine particles. The activity of coal processing and steel plants has been responsible for alterations in the air quality in some areas of the State of Rio Grande do Sul. In particular, the counties of Charqueadas and Sapucaia do Sul, located in the Baixo Jacuí Region, have shown problems with particulate contamination.[7,8] In both counties there are anthropogenic sources with emissions that have produced alterations in the air quality (steel industry and coal-fired power station). In Sapucaia do Sul, the main source of atmospheric pollutants is the Riograndense Steel Plant but heavy vehicular traffic was also verified at the place where the sampling was done.

The main purpose of this work is to study the chemical composition of the atmospheric particles in Charqueadas and Sapucaia do Sul , associate these data with the size of the particles and wind direction and identify and confirm the anthropogenic sources.

STUDY AREA

The area studied included the districts of Charqueadas (Figure 1a) and Sapucaia do Sul (Figure 1b) in the State of Rio Grande do Sul, Brazil. Both districts, as mentioned above present several economic activities that lead to significant emissions of particulate matter in the atmosphere. The sampling points were established with the aid of a GPS and the coordinates were as follows for Charqueadas (29°57’12,8”S and 51°37’21,4”W), west of the steel plant and southeast from the power plant. In this area there are mineral coal reserves and a coal mine, power plant and steel plant, all in operation. For Sapucaia do Sul the coordinates were 29o49’11,4”S and 51o09’39,0”W. The sampling site is situated 1km east of the main highway BR-116 and 1,7km northwest of the steel plant. The economic activity in this area includes metallurgy, leather and other industries. The general area studied has subtropical humid climate (Cfa type) with average temperatures between -3°C and 18°C for the coldest month and above 22°C for the hottest month. The total precipitation is superior to 1200mm and is well distributed through the year.

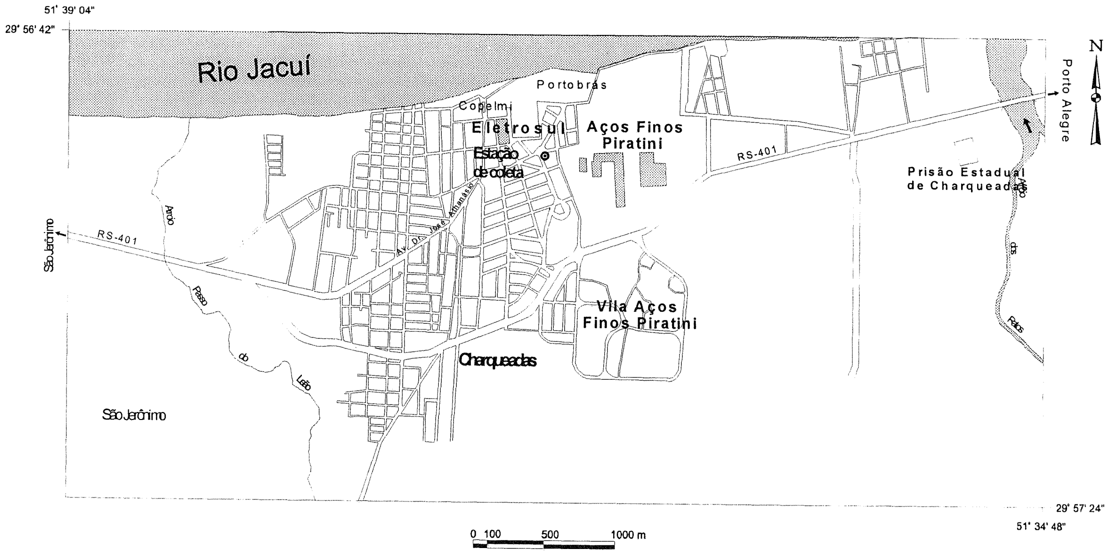


Figure 1a. Map Illustrating Sampling Site in Charqueadas, RS, Brasil

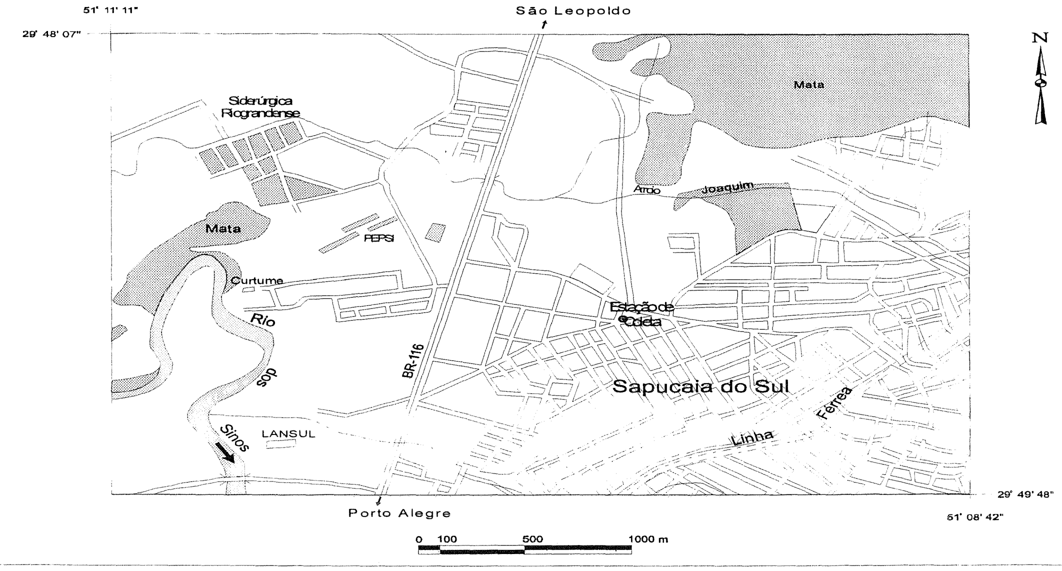


Figure 1b. Map Illustrating Sampling Site in Sapucaia do Sul, RS, Brasil

EXPERIMENTAL PROCEDURE

Sampling

High Volume Samplers (Hi Vol type) were used to collect atmospheric particles <100mm. The sampler consisted of a filter bearer that aspirated air through a filter with a flow varying between 1,13 and 1,70m3/min for 24 hours.[9] The samples were collected using 0,4µm pore size polycarbonate membrane filters.1-10. Eight samples were collected at each site leading to a total of sixteen (16) for the period from May 1997 to May 1998.

Analysis of samples using a scanning electron microscope equipped with energy dispersive x-ray microanalysis

The samples were analyzed with a LEO 440 Scanning Electron Microscope (SEM) with an energy dispersive x-ray detector (EDX) and an Inquant image analyzer at the Center of Mineral Technology (CETEM) in Rio de Janeiro. The specifications for EDS (energy dispersion spectroscopy) were as follows: Link ISIS L300 SiLi Pentafet detector, ATW ultrafine window with resolution of 133 eV for 5,0keV with ZAF correction, focal distance of 25mm, approximately 4000 counts for 5 seconds with a Co analytic window.

The procedure for the obtention of the EDS analysis consisted basically of the image of the retro-dispersed electrons (BSD), processing of the image for the individuality of the grains, EDs analysis of each one of the identified grains and storage of the results.

The quantification of the elements from the spectra took into consideration ZAF corrections (atomic number and mass fluorescence) and used the program SEMQUANT, Oxford ISIS 3. The elements analyzed were the following: Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn and Pb. The perimeter of the particles was defined and the average diameter was calculated. It is important to observe that the particle diameter used was obtained from microscopy and is not an average aerodynamic diameter.

Statistical analysis

The statistical treatment was carried out with a computer using the software Statistics for Windows 4.3™ and SPSS for Windows, first for Cluster Analysis followed by Factorial Analysis using the Principal Components Method.

Cluster analysis using the K method is not hierarchic and consists of grouping cases with similar profiles and a series of definite features. In the present study three stages were used for the grouping of elementary composition in the atmospheric particles: identification of the type of particles present in the aerosols (each type of particle was represented by a group – cluster), reduction of the volume of data without a significant loss of the data set and exclusion of particles that presented maximum seed points, not exceeding 10% of the data set. Only particles with diameter <10 were considered for cluster analysis. This corresponded to a total of 5057 particles from Charqueadas and 4913 particles from Sapucaia do Sul.

This analysis was applied to the elements Al, Si, S, K, Ca, Mn, Fe and Zn. Magnesium was excluded due to the maximum distance of the seed points. Factorial analysis through the principal component method was applied for Si, Al, Fe, Zn, Ca, S and Na.

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the general characteristics of the samples obtained in Charqueadas and Sapucaia do Sul, respectively. Properties such as average particle concentration, wind direction, wind speed, number of particles and average diameter.

Table 1. Genertal Characteristics of the Samples Collected in Charqueadas.

Filer	Sample date	Season date	Wind direction	Wind speed (m/s)	Average concentration ($\mu g.m^{-3}$)	Particle number	Average diameter (μm)
1	11/06/97	winter	NW	0,24	112	570	2,46
2	14/07/97	winter	SE	0,61	148	569	3,06
3	16/09/97	winter	NW	0,88	103	599	2,46
4	03/10/97	spring	SE	3,68	303	809	1,66
5	03/03/98	summer	NW	0,58	107	542	2,59
6	21/03/98	summer	SE	2,20	131	797	2,00
7	08/04/98	autumn	W	2,23	94,3	484	2,82
8	21/05/98	autumn	SE	0,96	206	702	2,34

Primary standard : 240 $\mu g.m^{-3}$ (Conama, 1992)
Secondary Standard : 150 $\mu g.m^{-3}$ (Conama, 1992)

Table 2. General Characteristics of the Samples Collected in Sapucaia do Sul.

Filer	Sample date	Season date	Wind direction	Wind speed (m/s)	Average concentration ($\mu g.m^{-3}$)	Particle number	Average diameter (μm)
1	11/06/97	Autumn	NW	0,60	139	646	2,58
2	14/07/97	winter	NW	1,39	300	569	2,37
3	16/09/97	winter	E	1,01	208	606	2,91
4	03/10/97	spring	E	5,71	244	634	2,45
5	03/03/98	summer	SE	0,59	121	490	2,33
6	21/03/98	spring	W	2,17	92,8	761	2,73
7	08/04/98	Autumn	W	3,50	276	484	2,43
8	21/05/98	Autumn	NW	0,26	290	759	2,24

Primary standard : 240 $\mu g.m^{-3}$ (Conama, 1992)
Secondary Standard : 150 $\mu g.m^{-3}$ (Conama, 1992)

Eight different filters were used at both locations. An average size of <10μm prevailed and accounted for more than 98% of the total of all particles (1-100μm) Figure 2 and 3 show the average percentage values for the elements studied found at the two sampling sites.

Figure 2. Average Percentage of the Elements Studied for Each Filter for Charqueadas.

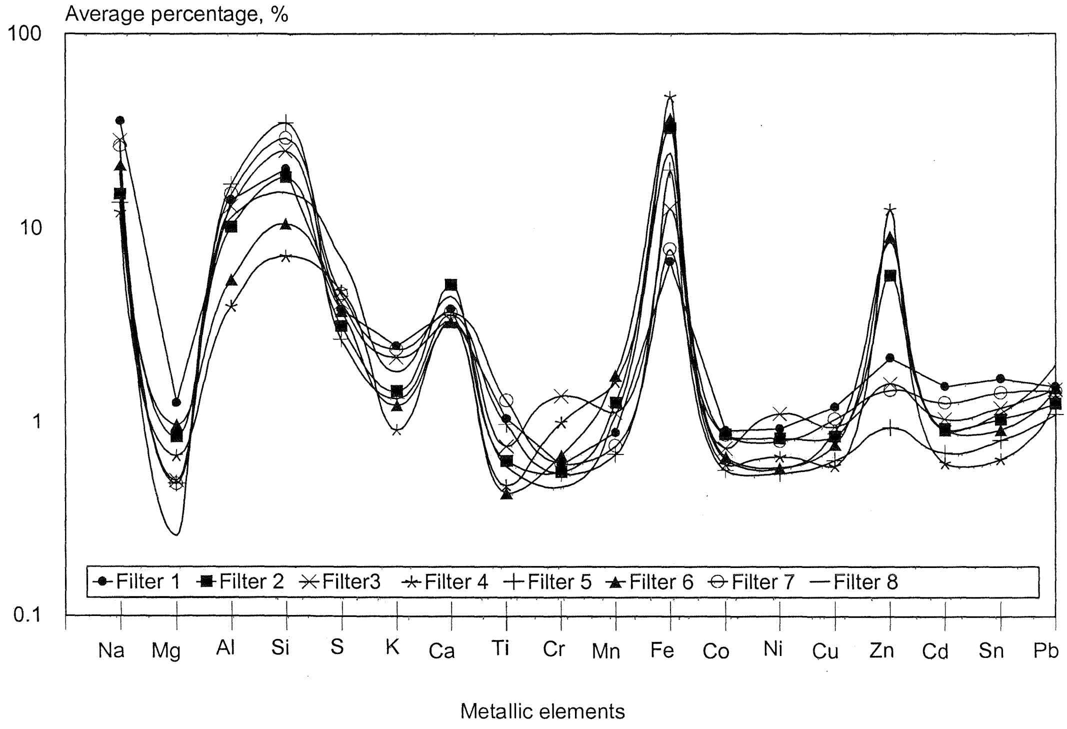
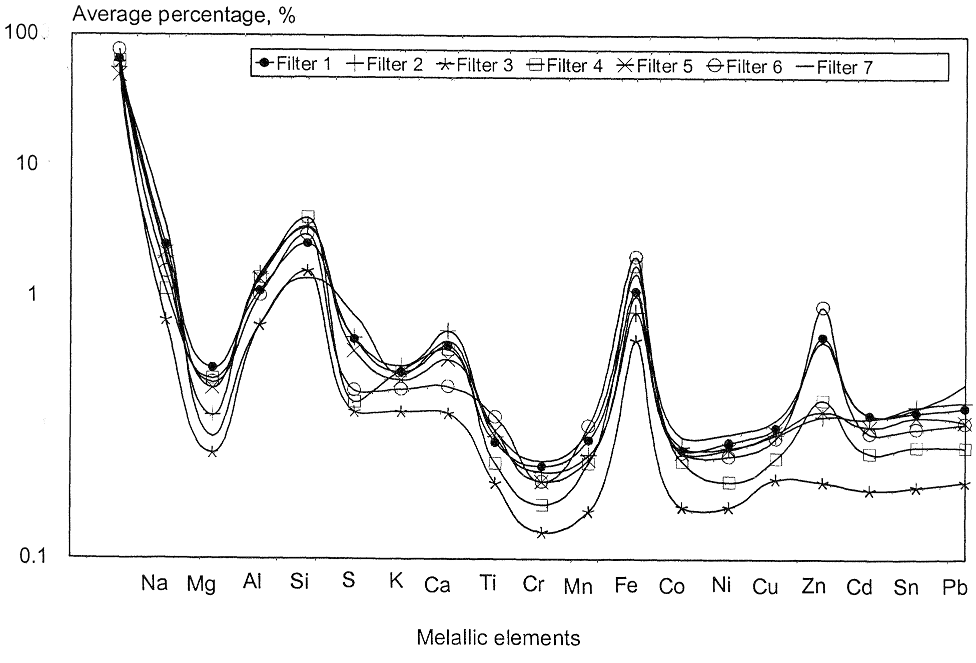


Figure 3. Average Percentage of the Elements Studied for Each Filter for Sapucaia do Sul.



For the case of Charqueadas, higher particulate concentrations were observed for the SE direction, corresponding to filters 4 (303μgm^{-3}) and 8 (206μgm^{-3}) for spring (October 3, 1997) and autumn (May 21,1998), respectively. The value observed for filter 4 was above that allowed by Brazilian Legislation, 240μgm^{-3} for 24 hours.[9]

For these filters, as well as for filters 2 and 6 that correspond to the direction of the SE quadrant, the percentage of Fe and Zn were higher, while Mn was lower (Figure 2). The steel plant is located in the SE direction in relation to the sampling station and this fact in addition to the higher concentration of the two elements and particularly Fe, point to the steel plant as the contamination source for this type of particulate.

The filters 1 (112mgm-3), 3 (103mgm-3) and 7 (94,3mgm-3)showed smaller concentrations than the others, however, the preferential NW/W direction of the winds and the presence of Si and Al point to the coal power plant as the main anthropogenic source (Figure 2).Particles of Al/Si (aluminosilicate) and Si (quartz) have been identified in ashes derived from coal combustion by several authors.[11,12] They consist mainly of fine particles in spherical form, being characterized as fly ash.[10,11,13]

S presented a similar behavior in all filters studied, except for filter 8 where the wind direction was in the SE quadrant with respect to the receptor source and the S percentage was higher. In this case both anthropogenic sources in Charqueadas are responsible for the presence of S, however higher emissions of SO_2 are probably from the steel plant.

In Sapucaia do Sul high particulate concentration was verified for filters 2 (300μgm^{-3}), 7 (276μgm^{-3}) and 8 (290μgm^{-3}). In all three case the concentration was above the air quality stabdard for particulates required by Brazilian legislation (240$\mu gm^{-3)}$ for 24 hours.[9]

The elements Fe-Zn/Mn and Si-Al were identified in different wind directions, probably indicating that several local sources were responsible for these emissions. However, filters 6 and 8 that correspond to the directions W/NW, respectively, showed higher percentages of Fe, Zn and Mn (Figure 3) probably indicating that the emissions originated from Riograndense Steel Plant.

Silicon and aluminum showed higher percentages for filters 2,4 and 5 in the directions NW, E and SE with reference to the receptor source, indicating contribution from several anthropogenic sources (Figure 3). The experimental results obtained for Sapucaia do Sul did not allow a clear identification of the anthropogenic contribution. The particles in this region are more heterogeneous and due to several sources such as automobile exhausts, steel plants, refineries, etc. Besides, the sampling point was close to the BR-116 Highway with intense automobile traffic. Further studies are need

Cluster Analysis

Cluster analysis was applied to the experimental data obtained for atmospheric particles (<10µm) collected at both sites. The total number of particles considered corresponded to 5057 for Charqueadas and 4913 for Sapucaia do Sul.

Table 3 summarizes the results obtained for Charqueadas, where six different groups of particles were obtained. Group 1 was characterized by particles rich in silicon (69,0%). Group 2 was characterized by particles rich in Ca (33,0%), S (19,0%) and associated with Na (19,0%).Group 3 contained large amounts of Na (48,o%) . Group 4 , that may be called the aluminosilicate group contained 33,0% Si and 26,0% Al. Group 5 contained mainly Fe (44,0%) and Zn (16,0%) and Na (19,0%). Group 6 contains mainly iron (73,0%) and the Fe particles are very small and generally present in spherical form.[10,11,13] For Sapucaia do Sul , cluster analysis also resulted in six groups (Table 4) and they were similar to the ones found for Charqueadas.

Table 3. Element Centroids Determined for Particle Samples from Charqueadas.

Elements (%)	Group 1: * Si	Group 2: * Ca e S	Group 3: * Na	Group 4 : * Al e Si	Group 5: * Fe e Zn	Group 6 : * Fe
Total number cases	417	359	804	1515	1157	805
Al	6,8	4,2	6,9	26	1,9	0,9
Si	69,0	5,4	9,0	33,0	3,4	1,7
S	1,8	19	6,2	3,0	3,3	1,2
K	1,4	1,4	2,4	2,7	0,8	0,4
Ca	0,8	33,0	2,4	1,6	1,7	0,9
Cr	0,4	0,5	1,0	0,5	1,0	0,9
Mn	0,4	0,7	1,2	0,6	2,2	1,6
Fe	2,9	4,6	7,7	6,3	44	73,0
Co	0,5	0,7	1,0	0,6	0,7	0,7
Ni	0,5	0,7	1,3	0,7	0,6	0,6
Cu	0,7	0,9	1,4	0,8	0,7	0,5
Zn	1,0	2,8	3,7	1,6	16	5,5
Sn	0,8	1,5	1,8	1,1	0,8	0,5
Pb	1,0	3,0	2,1	1,2	1,6	0,8
Na	11	19,0	48,0	17,0	19,0	9,4

**Rich particle*

Table 4. Element Centroids Detaremined for Particle Samples from Sapucaia do Sul.

Elements (%)	Group 1: * Si	Group 2: * Ca e S	Group 3: * Fe e Zn	Group 4: * Fe	Group 5: * Na	Group 6: * Al e Si
Total number cases	735	254	427	661	651	2185
Na	9,0	21,6	25,7	15,4	46,4	14,3
Al	9,4	2,3	1,5	2,3	4,7	16,1
Si	66,2	3,7	3,8	5,3	8,7	29,4
S	1,3	21,9	3,5	1,5	6,9	2,1
K	3,2	1,3	1,2	0,7	2,2	2,6
Ca	1,2	29,1	0,7	1,0	2,9	2,5
Cr	0,3	0,5	0,4	0,4	0,6	0,3
Mn	0,4	0,6	1,6	1,9	1,0	0,5
Fe	2,9	2,3	23,2	54,2	7,4	7,9
Co	0,5	0,7	0,6	0,7	0,9	0,5
Ni	0,4	0,7	0,6	0,4	1,1	0,5
Cu	0,6	0,8	0,8	0,8	1,6	0,6
Zn	1,1	2,5	28,8	8,7	5,9	1,7
Sn	0,8	1,8	0,9	0,6	1,7	0,9
Pb	0,7	3,3	1,5	1,2	2,2	0,8

**Rich particle*

Group 1 contained manily silicon (66,2%) and group 2 was characterized by Ca (29,1%) , S(21,9% and Na (21,6%). Group 3 consisted mainly of Fe (23,2%) and Zn (28,8%) while group 4 was mainly iron (54,2%Fe). Group 5 consisted predominantly of Na (46,4%) and group 6 was the aluminosilicate group (16,1%Al and 29,4%Si).

The results from the two sampling sites were similar, However, particles containing Fe and Zn were present in larger numbers in Charqueadas , while in Sapucaia do Sul the Si and Si-Al groups prevailed.

The iron particles in pure form and also associated with Zn prevail in small particle size (<2,5μm) and are present in spherical form. This morphology sioze was also verified by other authors.[2,13] Teixeira and coworkers confirmed the presence of iron particles in Charqueadas and pointed the steel plant present in the region as the possible source of emission. This hypothesis was confirmed visually by the emission of red smoke, indicating the presence of iron oxides.

The most abundant among the analyzed particles were those containing Al and Si (alunimosiulicates). These particles (~66-69%Si) were identified as quartz in submicron size and originated from coal combustion.[10]

The particles rich in S an Ca may originate from various sources, including coal combustion, when $CaSO_4$ is present in fly ash.[12] In the case of Charqueadas, the particles rich in Ca and S originate from the coal power plant and the steel plant, both using fossil fuels for energy generation.

The distribution of particle size in relation to elementary composition is illustrated in Figures 4 and 5 for the sampling sites of Charqueadas and Sapucaia do Sul, respectively.

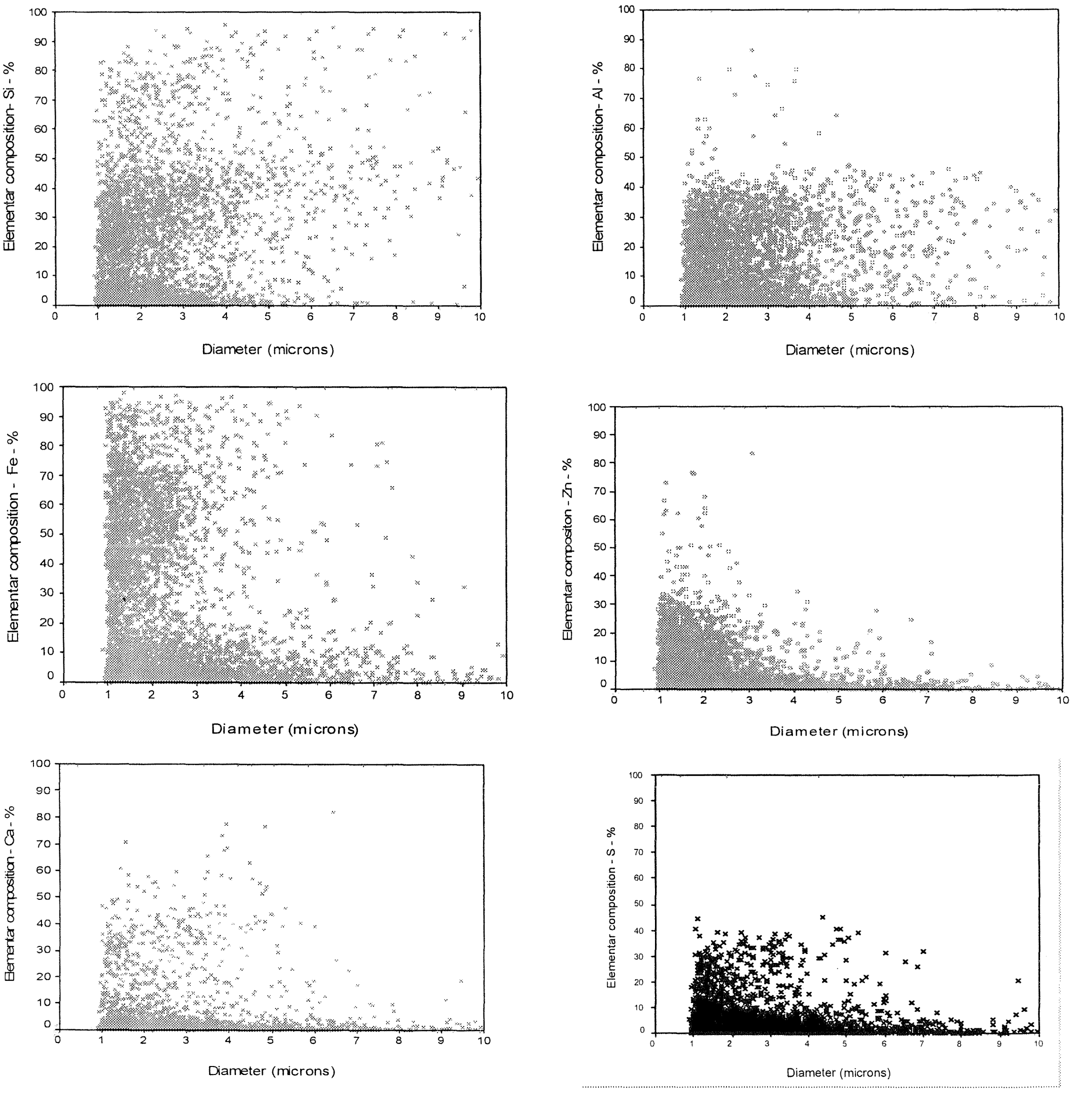


Figure 4. Variation of Particle Diameter with Elementary Composition – Charqueadas

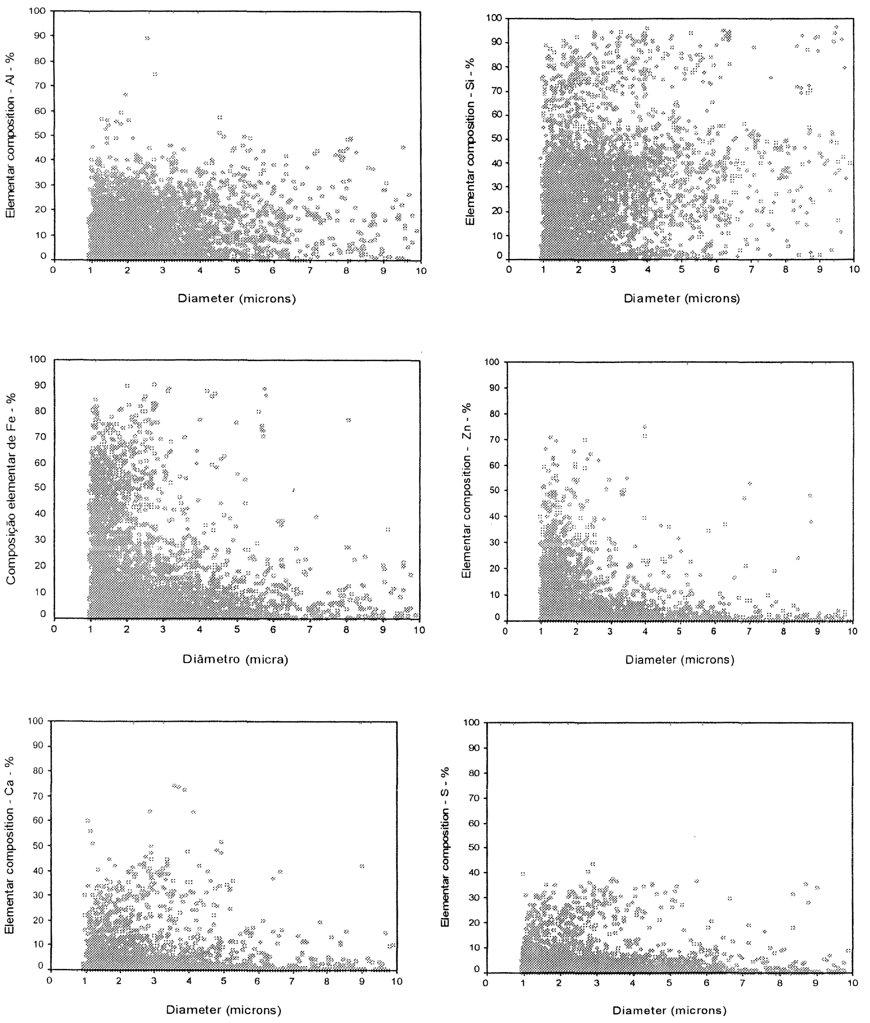


Figure 5. Variation of Particle Diameter with Elementary Composition-Sapucaia do Sul

Of the elements studied (Al, Si, Fe, Zn, Ca and S) all were found in higher concentration in the finer particles (2,5μm), indicating anthropogenic sources. The contribution of the coarse particle fraction (2,5 -10μm) was less significant and was attributed to the soil natural source.

Factorial Analysis

The statistical methods were carried out in the computer using the *Statistics for Windows* 4.3 ™ software. The procedure used applied the factor analysis technique through the principal component method to the data sets obtained through cluster analysis for Charqueadas and Sapucaia do Sul.

For Charqueadas, these sets resulted in three factors associated with characteristic eigenvalues >1,0., that synthesized, after the application of the Varimax Rotation normalized to the factor loadings of 76,16% of the total variance. The factor loadings for varables studied in the particle samples from Charqueadas are shown in Table 5.

Table 5. Factor Loadings for the Variables \studied in Particle Samples from Charqueadas.

	Factor 1	Factor 2	Factor 3
Na	0,04	0,02	*0,77*
Al	*0,79*	-0,16	-0,16
Si	*0,82*	-0,20	-0,20
S	0,00	*0,87*	0,01
Ca	0,00	*0,90*	-0,18
Fe	*-0,79*	-0,27	-0,22
Zn	*-0,64*	-0,13	-0,08
Variância total (%)	33,58	24,70	17,88

* *Factor loading* ≥ 0,50

The first factor (33,58 of the total variance) was attributed to the elements that presented a higher frequency in the group of data. This factor had higher loads for Si, Al, Fe and Zn. For the last two elements the signs presented were the opposite. The results show that the two different groups, Si-Al and Fe-Zn, originated from two different sources, from the power plant and the steel plant, respectively. These elements had sown predominance of more than 50% in the fine fraction (2,5µm) as was seen in Figure 5. The second factor, with high factorial load for S and Ca, explained 24,70% of the total variance of the data. This factor is represented by original particles of the two local sources, that are responsible for the emissions of S. The third factor, characterized by particles containing Na revealed the contribution of natural sources.

For Sapucaia do Sul, the data sets resulted in two factors associated with characteristic eigenvalues >1,0 that synthesized after application of the Varimex Rotation normalized to the factor loadings of 59,01% of the total variance. The factorloadoings fro the variables studied in particle samples from Sapucaia do Sul are shown in Table 6.

Table 6. Factor Loadings for the Variables Studied in Particle Samples from Sapucaia do Sul.

	Factor 1	Factor 2
Na	0,44	0,34
Al	*-0,67*	-0,16
Si	*-0,79*	-0,28
S	0,14	*0,90*
Ca	-0,06	*0,84*
Fe	*0,64*	-0,39
Zn	*0,69*	-0,12
Variância total (%)	31,3	27,8

* *Factor loading* ≥ 0,50

The first factor, characterized by the higher factorial loads for Si and Alk and with negative signs for Fe and Zn, explained 31,29% of the total variance. In spite of the fact that the elements presented opposite signs for this factor, as in Charqueadas, indicating two different anthropogenic sources, it was not possible to clarify the origin of the emissions of these species.In Sapucaia do Sul, the collector was located in a place of intense vehicular traffic, being subject to a significant influence of mobile sources. Figure 6 shows the relation between wind direction and the average composition for the elements characterized by cluster analysis of the eight filters used for collection in Charqueadas. The presence of Fe in high concentration in the SE direction point to the steel plant as the emission source, while the high concentrations of Si and Al in the NW direction indicate the coal power station plant as the source of emissions.

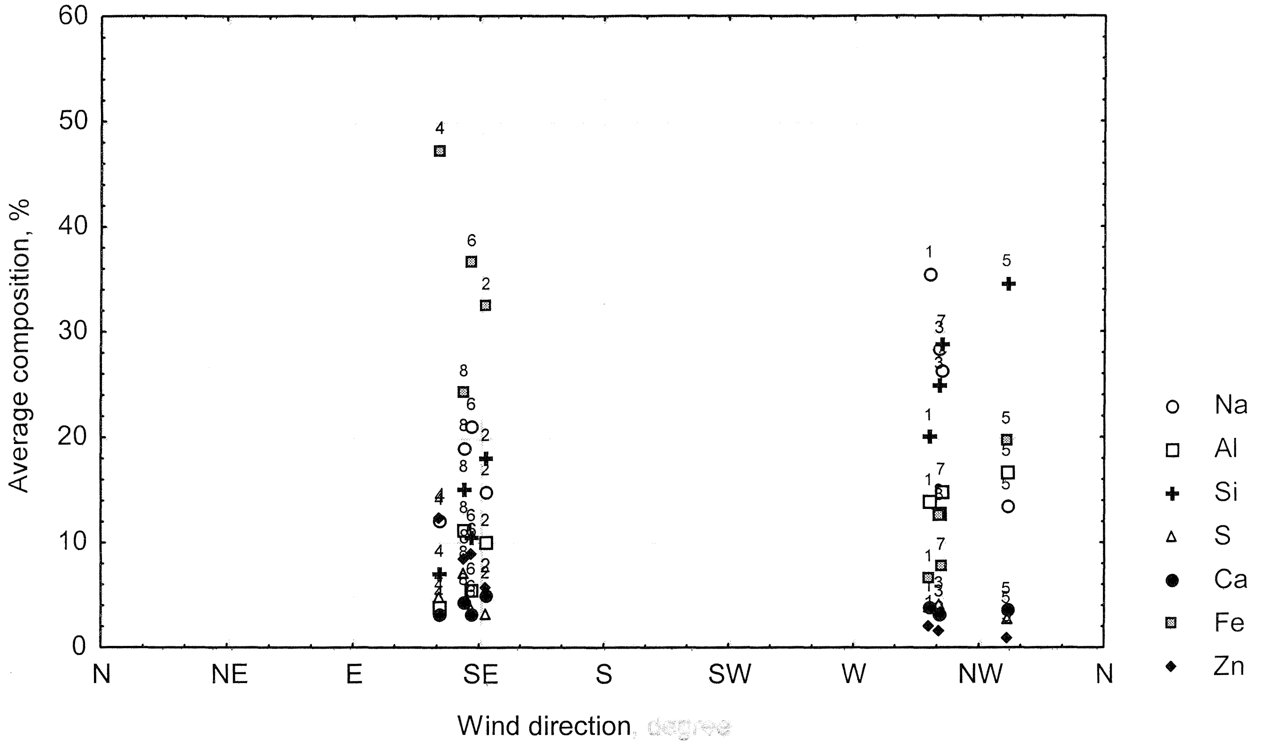


Figure 6. Relation between Wind Direction and Average Composition for Charqueadas for the Eight Filters Employed.

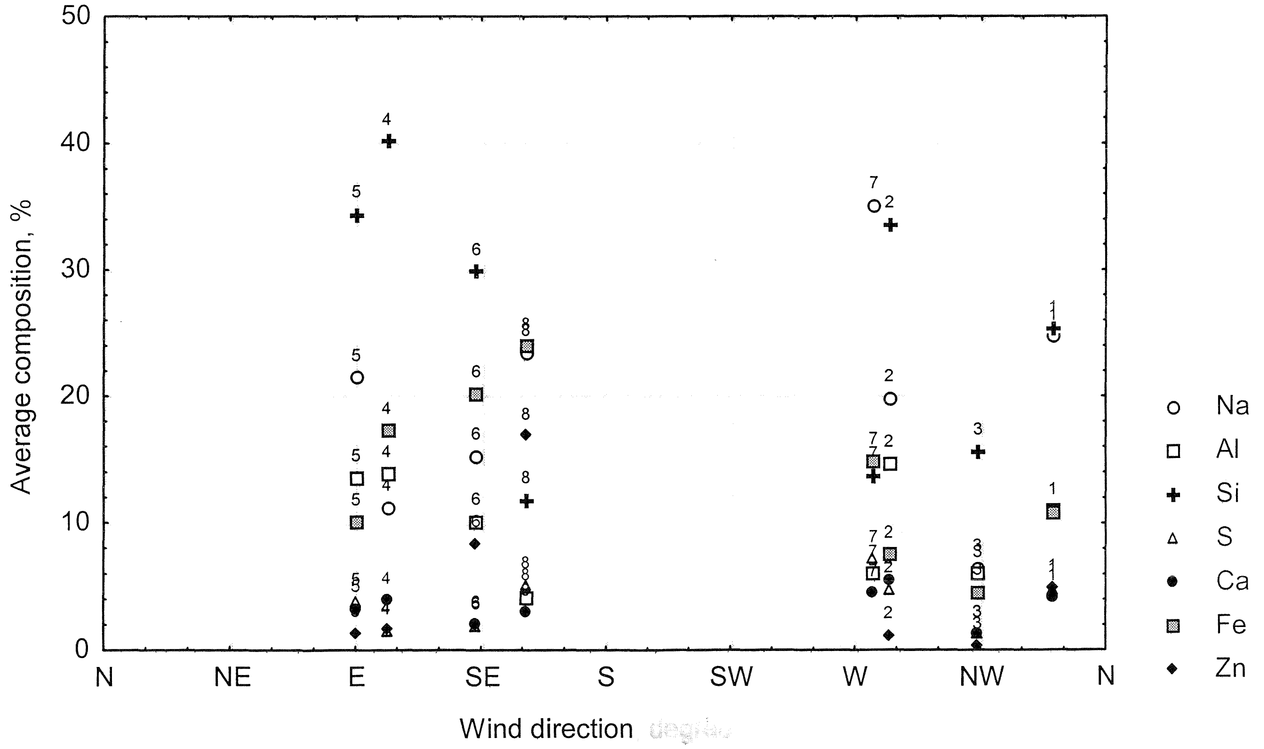


Figure 7. Relation between Wind Direction and Average Composition for Sapucaia do | do Sul for the Eight Filters Employed.

Figure 7 shows the average composition and wind direction for Sapucaia do Sul. As can be seen, the samples containing Fe and Zn concentrate in the SE direction, where the steel plant is located. On the other hand, the Si-Al samples are more dispersed, indicating the contribution of several sources.

CONCLUSIONS

The experimental results obtained in this study showed that the quality of air in Charqueadas and Sapucaia do Sul was affected mostly by fine atmospheric particles (<2,5μm)

Cluster analysis indicated the presence of six distinct groups in both locations: Fe-Zn, Fe, Si-Al, Si, Ca –S and Na.

Factorial analysis through the Principal-Components Method applied to the data sets from cluster analysis resulted in tghree factors for Charqueadas and two for Sapucaia do Sul.

For Charqueadas, Factorial analysis indicated that Fe and Zn have anthropogenic origin and the steel plant can be considered as the responsible source. Particles rich in aluninosilicates and quartz were identified as fly ash originating from the coal power plant. Both the steel plant and the power plant in Charqueadas also contributed to the formation of particles containing Ca and S.

For Sapucaia do Sul it was not possible to determine the source of Si-Al rich particles. They may be due to vehicles, suspense matter or other sources. The steel plant was characterized as the source of particles rich in Fe and Zn and for the case of wind in the W and NW directions during the sampling days, the steel plant was also the source of the emission of particles rich in Ca-S. For other wind directions it was not possible to define the source, however one possibility being automobile traffic. The identification of anthropogenic sources in Sapucaia do Sul requires additional studies.

ACKNOWLEDGMENTS

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REFERENCES

1. J.E. Post and P. Buseck, *Environ. Sci. Technol., 18*, 35-42 (1984).
2. C. Xchoffer, V.P. Bernard, R. Van Grieken and L. Van der Auwera, *Environ.Sci. Technol.,25*, 1470-1478 (1991).
3. C.M. Romo-Kröger, *Environmental Pollution, 68*, 161-170 (1990).
4. P.Artaxo, P. Oyola and R. Martinez, *Nucl. Instr.Meth. Phys.Res., B150*, 409-416 (1999).
5. F. Echalar, P. Artaxo, V. Martins, M.Yamasoe and F. Gerab, *J. Geophys. Res., 103(24D)*, 31849-31864 (1998).
6. P. Artaxo, E.T. Fernandes, J.V. Martins, M.A. Yamasoe, P.V. Hobbs, W. Maenhaut, K.M. Longo and A. Castanho, J. Geophys. Rers., 103(24D),31837-31847 (1998).
7. E. C. Teixeira, D. Migliavacca, J.D. Sanchez and J. Fachel, *Ciência e Natura (Santa Maria), 21*, 29-50 (1999).
8. F. G. Carvalho, A. Jablonski and E.C. Teixeira, *Química Nova, 23(5)*, 614-617 (2000).
9. CONAMA, Resolução Conama No. 005 de 15 de Junho de 1989, *Publicações Conama*, Brasília, DF, 1992.
10. V.N. Malderen, R. van Grieken and N.V. Bufetov, *Environ. Sci. Technol., 30*, 312-321 (1996).
11. D. J. Swaine and F. Goodarzi, *Environmental Aspects of Trace Elements in Coal*, Kluwer Academic Publishers, Amsterdam, 1995, 312pp.
12. E.C. teixeira, J.C. Samama and A. Brun, *Environmental Technology, 13(10)*,995-1000 (1992).
13. K.A., Katrinak, J.R. Anderson and P.R. Buseck, *Environ. Sci. Technol., 29*, 321-329 (1995).

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PRESENCE OF MERCURY IN PETROLEUM

PRESENÇA DO MERCÚRIO NO PETRÓLEO

João Marcos Hohemberger; Carlos Pérez Bergmann and Lavinel G. Ionescu*

Departamento de Materiais, Escola de Engenharia,
Universidade Federal do Rio Grande do Sul
Porto Alegre, RS – BRASIL.

ABSTRACT

The present article is a review of current knowledge of the presence of mercury in petroleum and natural gas. Effect of mercury on petrochemical processes and its removal are also discussed.

KEYWORDS: **Mercury, Petroleum, Natural Gas, Mercury Removal, Petrochemical Processing**

RESUMO: ***O presente artigo é uma resenha sobre a presença do mercúrio no petróleo e no gás natural. O efeito do mercúrio sobre processos petroquímicos e a sua remoção de hidrocarbonetos é discutida.***

Palavas Chave: Mercúrio, Petróleo, Gás Natural, Remoção de Mercúrio, Processamento Petroquímico.

Introdução

Varias espécies de mercúrio estão presentes no petróleo e no gás natural, geralmente em quantidades muito pequenas. O mercúrio pode estar presente na forma de elemento livre, Hg, sulfeto de mercúrio, HgS, cloreto mercuroso, Hg_2Cl e vários compostos orgânicos de mercúrio. Os complexos de mercúrio e enxofre podem ser derivados de sulfetos, tiol, tiofeno ou mercaptanas. [1 – 11]

Em geral a análise de compostos de mercúrio em petróleo é muito difícil de efetuar, especialmente pela dificuldade de amostragem e pela presença em quantidades muito pequenas. A Tabela I apresenta alguns compostos orgânicos de mercúrio e o respectivo ponto de ebulição.

*** To whom correspondence should be addressed.**

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Tabela I – Pontos de ebulição de alguns compostos de mercúrio (ref. 4)

Compostos de Hg	**Ponto de ebulição (°C)**
Hg^0	357
$(CH_3)_2Hg$	96
$(C_2H_5)_2Hg$	170
$(C_3H_7)_2Hg$	190
$(C_4H_9)_2Hg$	206

A Tabela II resume a solubilidade de compostos comuns de mercúrio em hexano e a Tabela III mostra alguns valores representativos para a concentração de mercúrio em petróleo bruto e em derivados de petróleo comparados com um valor médio de 1,5 ppm (N=76).

Tabela II. Solubilidade de alguns compostos de mercúrio em hexano (ref. 4)

Espécie	**Solubilidade (ppb)**	**Temperatura (°C)**
Hg^0	1,200	27,5
$HgCl_2$	11,500	27,5
CH_3HgCl	>1.000.000	20,0
$(CH_3)_2Hg$	∞	

Tabela III. Concentração total de Hg em petróleo e seus derivados (ref. 4)

Tipo	*N*	Hg (ng/g)	
		Média	Desvio padrão
Petróleo bruto	76	1.505	3.278
Frações leves de petróleo	39	3.009	4.140
Frações pesadas de petróleo	37	1,20	1,49
Condensado total	18	3.964	11.665
Condensado leve	10	7.113	15.240
Condensado pesado	8	20,4	19,7
Destilados leves	14	1,32	2,81
Óleos combustíveis	32	0,67	0,96
Asfalto	10	0,27	0,32

N= 76, valor médio para petróleo bruto (1,5 ppm, N=76)

As Figuras 1 e 2 ilustram respectivamente a quantidade total de mercúrio em amostras de petróleo bruto e nafta provenientes de diversos países. Os resultados foram obtido usando vários métodos de análise, incluindo espectrometria de massa, espectrometria atômica de emissão, análise de ativação de nêutrons, cromatografia líquida de alta pressão e outros.

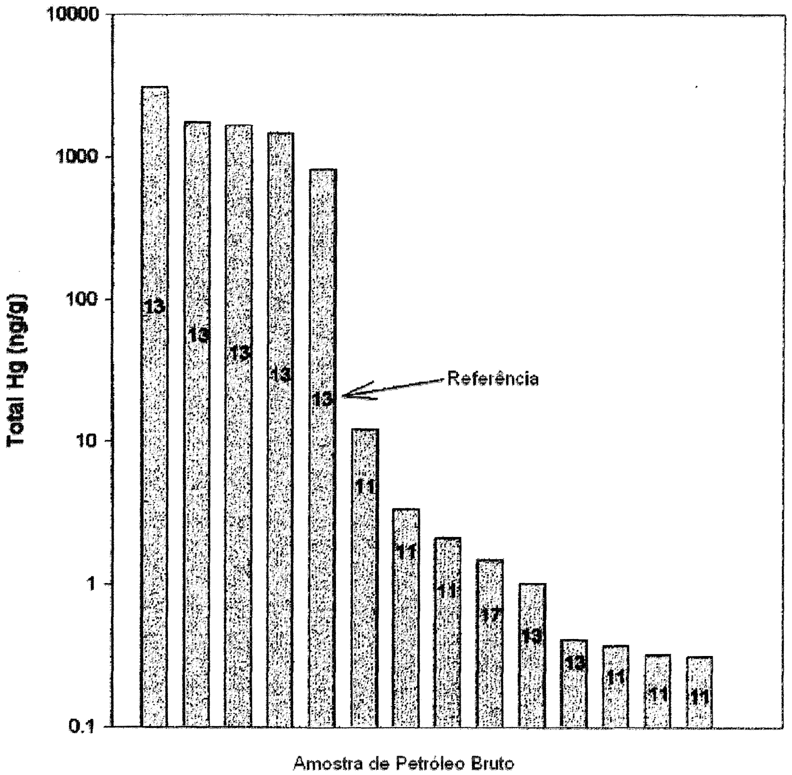

Figura 1. Concentração total de mercúrio em amostras de petróleo bruto. (ref. 4)

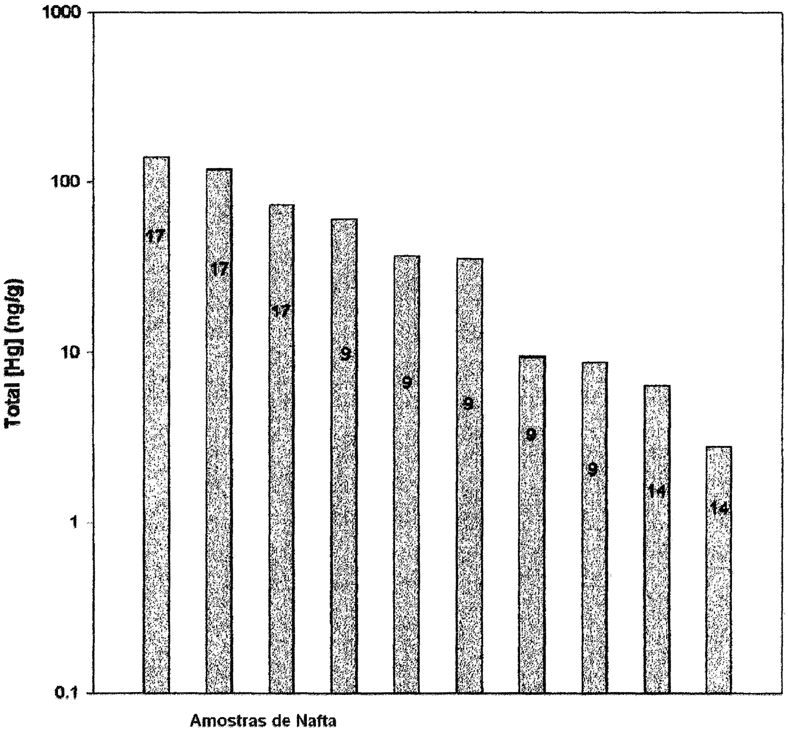

Figura 2. Concentração total de mercúrio em amostras de nafta. (ref. 4)

Efeitos adversos do mercúrio no processamento petroquímico

O mercúrio tem vários efeitos nocivos nas operações que envolvem processamento de gases:

1. O mercúrio deposita-se em equipamentos criogênicos e pode causar fraturas, especialmente nas soldas do trocador de calor de alumínio. Existem muitos exemplos de falhas em caixas frias em plantas de processamento de gás e correntes de craqueamento de etileno. A introdução de caixas frias projetadas para resistir ao mercúrio e uso de sistemas de remoção de mercúrio diminuem drasticamente este tipo de acidentes que podem levar a grandes prejuízos econômicos.[1 - 4]
2. A mercúrio afeta de maneira negativa vários processos na petroquímica. Plantas de gás usadas para industria química, especialmente a preparação de olefinas, etileno, aromáticos e MTBE, correm risco, não somente nos aspectos que tangem ao equipamento, mas também o envenenamento de catalisadores.
3. O mercúrio contamina na maioria dos processos de tratamento, incluindo peneiras moleculares, unidades de dehidratação com glicol e sistemas gasosos de eleiminação de aminas. É muito difícil o tratamento dos líquidos gerados pois, é muito difícil regenerar os sistemas de remoção e dispor os efluentes.
4. Materiais que adsorvem o mercúrio no tratamento de gases ou líquidos constituem dejetos muito perigosos para os operadores de plantas, tendo em vista o armazenamento e eliminação dos mesmos.
5. A deposição do mercúrio no equipamento representa riscos à saúde e à segurança dos trabalhadores em manutenção, operação e inspeção.
6. Lodos contendo mercúrio que provem do tratamento de água, separadores, dessalinizadores e trocadores de calor apresentam resíduos altamente tóxicos, difíceis de armazenar e dispor.
7. Efluentes aquosos contendo concentrações altas de mercúrio devem ser tratados antes da sua descarga e isto representa um custo muito alto na operação das plantas.

Aspectos envolvendo a saúde e a segurança

Os aspectos mais críticos envolvendo a saúde e a segurança dos trabalhadores na petroquímica envolve a exposição dos mesmos a vapores de mercúrio e absorção de dialquilmercúrios através da pele. O mercúrio e seus compostos são neurotoxinas. A inspiração de vapor de mercúrio, a ingestão de sais iônicos de mercúrio ou a absorção de compostos de mercúrio através da pele resultam eventualmente em disfunções neurológicas. O período de tempo entre o contato com o mercúrio e o aparecimento de sintomas varia muito e depende do tipo das espécies de mercúrio absorvidas e da magnitude da exposição. Exposição crônica a vapores de mercúrio leva a anomalias psicológicas (excitabilidade), perda de memória, insônia e depressão e sintomas físicos (fraqueza, fadiga, anorexia e perda de peso). No caso mais avançado da doença aparecem tremores. Doses altas de mercúrio causam falha total da função renal. Alguns valores típicos de mercúrio encontrados em tecidos biológicos estão ilustrados na Tabela IV.

Tabela IV. Valores padrão de concentração de mercúrio em tecidos biológicos. (ref. 4)

Matriz	**Concentração**
Sangue	1–8 mg/l
Consumo de peixe	
Dieta sem peixe	2,0 mg/l
Duas refeições por semana	4,8 mg/l
Duas a quatro refeições por semana	8,4 mg/l
Urina	4–5 mg/l
Cabelo	2 mg/g
Consumo de peixe	
Uma vez por mês	1,4 mg/g
Uma vez cada duas semanas	1,9 mg/g
Uma vez por semana	2,5 mg/g
Uma vez por dia	11,6 mg/g

Mercúrio no Processamento Petroquímico

O mercúrio tem vários efeitos nocivos nas operações que envolvem processamento de gases. Sem dúvida, o problema começa pela quantidade de mercúrio presente na matéria-prima. Mercúrio líquido em contato com o alumínio pode causar falhas rápidas e sérias. Mercúrio presente até em quantidades muito pequenas no gás natural e no petróleo pode ser concentrado em sistemas de destilação criogênica. Se o mercúrio está presente na forma líquida (por exemplo, durante períodos de interrupção ou paradas das plantas) pode causar danos catastróficos em trocadores de calor de alumínio. As fraturas podem acontecer sem aviso e por causa do crescimento rápido de trincas através do *LME*. Não existe nenhuma técnica adequada e não-destrutiva para monitorar e proteger as instalações.[6 – 11]

Não só pelas conseqüências na integridade de equipamentos a presença de mercúrio pode ser preocupante. O mercúrio afeta de maneira negativa vários processos na petroquímica. Plantas de gás usadas para indústria química, especialmente a preparação de olefinas, etileno, aromáticos e MTBE, correm risco, não somente nos aspectos que tange ao equipamento, mas também o envenenamento de catalisadores. O mercúrio contamina a maioria dos processos de tratamento, incluindo peneiras moleculares, unidades de dehidratação com glicol e sistemas gasosos de eliminação de aminas. É muito difícil o tratamento dos líquidos contaminados gerados, pois, é muito difícil regenerar os sistemas de remoção e dispor o efluentes.[2 – 7]

A deposição de mercúrio no equipamento representa riscos à saúde e à segurança dos trabalhadores em manutenção, operação e inspeção. Da mesma forma, os efluentes aquosos contendo concentrações altas de mercúrio devem ser tratados antes da sua descarga, o que representa um custo muito alto na operação das plantas. Lodos contendo mercúrio que provêm do tratamento de água, separadores, dessalinizadores e trocadores de calor apresentam resíduos altamente tóxicos, difíceis de armazenar e dispor.

Efeitos adversos do mercúrio em equipamentos

Materiais que adsorvem o mercúrio no tratamento de gases ou líquidos constituem alvos muito perigosos para os operadores de plantas, tendo em vista o armazenamento e eliminação dos mesmos.

Sem dúvida, o principal risco à integridade de equipamento é dado pelos trocadores de calor. O mercúrio deposita-se em equipamentos criogênicos e pode causar fraturas, especialmente nas soldas de trocadores de calor de alumínio. Existem muitos exemplos de falhas em caixas frias em plantas de processamento de gás e correntes de craqueamento de etileno. A introdução de caixas frias projetadas para resistir ao mercúrio e uso de sistemas de remoção de mercúrio diminuíram drasticamente este tipo de acidentes que podem levar a grandes prejuízos econômicos.[1 – 11]

O sistema de resfriamento, no processo de separação de gases, usa um trocador de calor de placas de alumínio aletada. Há mais de seis décadas é conhecido o efeito devastador do mercúrio sobre alumínio, e a acumulação do mercúrio em plantas de gás natural e na indústria pode levar a conseqüências graves.

Normalmente, o núcleo do trocador é uma liga de alumínio Al3003, com cabeçotes, admissões e tubulações de alumínio Al5083 (a mais comum) ou Al6061, ligas de alumínio e magnésio. A presença de Si na forma de siliceto de magnésio pode contribuir para endurecer as ligas pelo envelhecimento. À temperatura ambiente, o alumínio pode conter em solução aproximadamente 1% de magnésio, porém, os trocadores de calor contêm 4,5%, formando fases metaestáveis que às vezes precipitam Al_3Mg_2. Este fenômeno é muito lento a temperaturas ambiente e criogênica, porém, se esta liga sofre processos de soldagem, a zona termicamente atingida (ZTA) apresenta uma diminuição considerável no fator *k* (fator de concentração de tensões), aumentando consideravelmente a sensibilidade ao ataque por metais líquidos.

Remoção do Mercúrio na Petroquímica

A Figura 12 apresenta um fluxograma típico de uma planta para olefinas. Existem trabalhos detalhados para a remoção de mercúrio no gás de craqueamento e de correntes líquidas executado pela Equistar Chemicals LP de Channelview, Texas nos Estados Unidos.

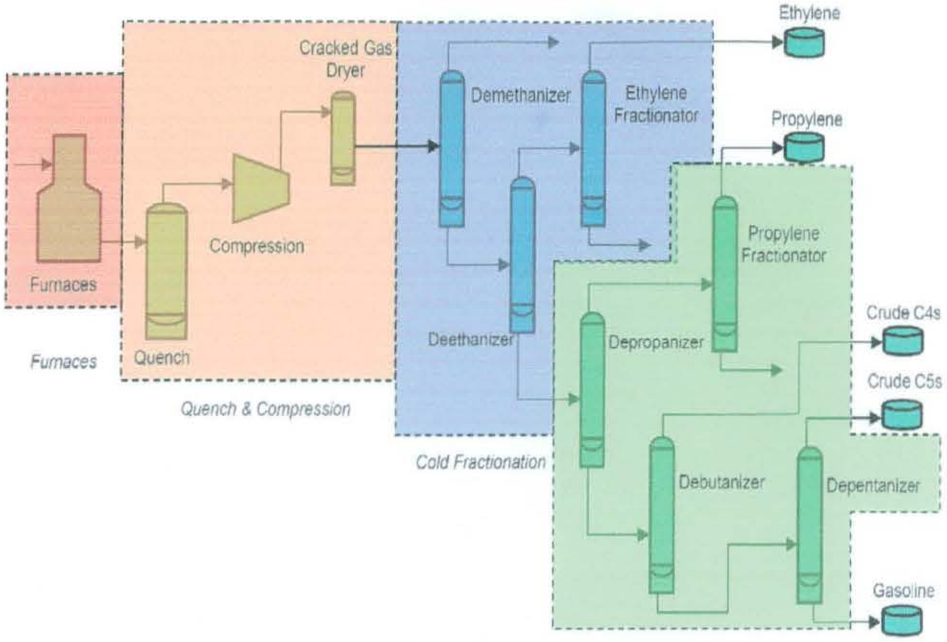

Figura 1 – Fluxograma típico de uma planta de olefinas. (ref. 2)

Em março de 2003, a planta número 2 da Equistar foi parada para manutenção programada, após funcionamento ininterrupto desde novembro de 1997. Foram encontradas quantidades significativas de mercúrio tanto na fase líquida quanto na fase vapor na parte de fracionamento frio da planta, região azul da Figura 1. A presença de mercúrio era esperada, baseada nas paradas anteriores de 1989 e de 1995, e devido ao conhecimento da presença de mercúrio na matéria-prima. A maior diferença entre a parada de 2003 e as outras foi a quantidade e o lugar onde foi encontrado o mercúrio. Nas anteriores, a maior parte do mercúrio foi encontrada em concentrações menores além da região de trocadores de calor. Durante a parada de 2003, o mercúrio foi encontrado em concentrações altas na região de fracionamento frio e compressão e expansão, áreas azul e amarela. As concentrações de mercúrio foram acima de valores recomendados e foram necessários esforços para a proteção do equipamento, pessoal e limitações à exposição dos trabalhadores. A *American Conference of Governamental Industrial Hygienists* estipulou um valor limite (*TLV – threshold limit value*) de 0,025 mg/m^3 de Hg para uma jornada de 8 horas e uma semana de trabalho de 40 horas. A concentração de mercúrio de fracionamento frio variou entre 0,010 mg/m^3 até 0,700 mg/m^3. A concentração alta de mercúrio causou atraso em um numero grande de atividades durante a parada.

O mercúrio é geralmente removido das correntes de hidrocarbonetos na fase líquida e gasosa usando leitos de adsorventes granulares com substratos como zeólita, carvão ativado, óxidos de metais e/ou alumina e um componente reativo, Ag, KI, CuS, ou outros sulfetos metálicos que ficam ancorados no suporte. Os direitos comerciais de leitos para a remoção de mercúrio dependem da natureza do suporte, do componente reativo e da maneira de ancoramento do último. A Tabela V resume alguns sistemas geralmente usados para a remoção de mercúrio.

Tabela V. Sistemas para remoção de mercúrio de hidrocarbonetos (ref. 11)

Reagente	**Substrato**	**Complexo**	**Aplicação**
Enxofre	Carbono, Al_2O_3	HgS	Gás
Sulfeto de metal	Carbono, Al_2O_3	HgS	Gás, líquido
Iodeto	Carbono	HgI_2	Líquido seco
Pd + H_2; sulfeto de metal	Al_2O_3	HgS	Líquido
Ag	Zeólita	Ag/Hg amalgama	Líquido leve e gás
Óxido / sulfeto de metal	Óxido	HgS	Gás, líquido

Existem vários tratamentos em escala comercial para remover o mercúrio de gás natural, petróleo e frações de corrente de craqueamento na indústria petroquímica. Algumas empresas que colocam à disposição equipamentos em escala comercial são *Equistar Chemicals LP Chanelview Texas* e *UOPLLC* Houston Texas, *Eastman* e OIKON *Ltd., Institute for Applied Ecology Vlade Prekrata*, Zagreb, Croácia.

REFERÊNCIAS

1. R. Coade and D. Coldham, " The Interaction of Mercury and Aluminium in Heat Exchangers in a Natural Gas Plants", International Journal of Pressure Vessels and Piping, 83, 336-343 (2006).
2. S. Coleman, J. Ries, D. Campbell and K.R. Clark, "Mercury Removal from Cracked Gas and Liquid Streams", presented at 2005 AIChE Spring National Meeting, 17th Annual Ethylene Producers' Conference, Session TA009 – Ethylene Plant Operations, Atlanta, GA, April 12, 2005.
3. T.Y. Yan, "A Novel Process for Hg Removal from Gas", Ind. Eng. Chem., 33,3010-3014 (1994).
4. S. Mark Wilhelm and N. Bloom, "Mercury in Petroleum", Fuel Processing Technology, 63, 1-27 (2006).
5. Z. Spiric, "Innovative Approach to the Mercury Control During Natural Gas Processing", Proceedings of ETCE 2001, Engineering Technology Conference on Energy, February 5-7, 2001, Houston Texas, USA.
6. S. J. Pawel, J.R. DiStefano and E.T. Manneschmodt, "Effect of Surface Conditions and Heat Treatment on Corrosion of Type 316L Stainless Steel IN A Mercury Thermal Convection Loop", ORNL/TM-2001/195, Report Prepared for the U.S. Department of Energy, Oak Ridge National Laboratory, Oak Ridge Tennessee, 2001.
7. J. S. Thompson and J. H. Pavlish, "Cryogenic Trapping of Oxidized Mercury Species from Combustion Flue Gas", Fuel Processing Technology, 65-6,167-175 (2000).

8. K. Ina and H. Koizumi, "Penetration of Liquid Metals into Solid Metals and Liquid Metal Embrittlement" Materials Science and Engineering",A387-389, 390-394 (2004).
9. Y.B. Xu, Y. Zhang, Z.G. Wang and Z.Q. Hu, "Fatigue and Fracture Behavior of Aluminum-Lithium Alloys at Ambient and Cryogenic Temperatures", Scripta Metallurgica et Materialia, 33(2), 179-183 (1995).
10. K. Crippen and S. Chao, "Mercury in Natural Gas and Current Measurement Technology" 1997 Gas Quality and Energy Measurement Symposium, February 3-5, Orlando, Florida, pp. 1-16.
11. S. Coleman, G. Nowowiejski and M. Blaschke, "Mercury Removal: An Overview", Paper presented at the 2005 AICHE National Meeting, Atlanta, GA, USA, April 10-14, 2005.

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MERCURY CORROSION OF CRYOGENIC ALUMINUM HEAT EXCHANGERS

A CORROSÃO POR MERCÚRIO EM TROCADORES DE CALOR CRIOGÊNICOS DE ALUMÍNIO

João Marcos Hohemberger, Carlos Pérez Bergmann and Lavinel G. Ionescu*

Departamento de Materiais, Escola de Engenharia,
Universidade Federal do Rio Grande do Sul
Porto Alegre, RS - BRASIL

ABSTRACT

The present article is a brief review of the current understanding of mercury induced Liquid Metal Embrittlement (LME), with particular emphasis on the corrosion and failure of aluminum cryogenic heat exchangers.

KEYWORDS: Aluminum, Mercury, Corrosion, Cryogenic Heat Exchangers, Liquid Metal Embrittlement (LME)

RESUMO

O presente artigo é uma breve resenha da corrosão por mercurio em trocadores de calor criogenico de alumínio. Em particular o mecanismo de corrosão por esfarelamento causado por metal líquido (LME – Liquid Metal Embritlement) é descrito em detalhe.

INTRODUÇÃO

O mercúrio, Hg, é um elemento conhecido desde a antiguidade. É encontrado livre na natureza em quantidades pequenas. O mineral mais comum é HgS, cinábrio, presente

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* To whom correspondence should be addressed.

E-mail: lavinel@ibest.com.br or lavinel@pop.com.br

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frequentemente em regiões vulcânicas. É produzido em quantidades significativas na Rússia, México, China, Argélia, Espanha, Peru e Califórnia (USA).

O mercúrio possui dois estados de oxidação, +1 e +2. É monovalente em compostos mercurosos, Hg_2O, óxido negro, e Hg_2Cl_2, e bivalente nos compostos mercúricos, HgO, vermelho ou amarelo, cloreto mercúrico ou sublimado e corrosivo, $HgCl_2$, sulfeto ou cinábrio ou vermelhão, HgS, e fulminato, $Hg(OCN)_2$, usado como detonador em explosivos.

Compostos orgânicos de mercúrio são muito raros na natureza. Os alquilmercúrios R_2Hg são encontrados em quantidades pequenas no petróleo.

O mercúrio é obtido por combustão do seu sulfeto ao ar livre e usado em termômetros, barômetros, bombas de vácuo, lâmpadas e retificadores a vapor de mercúrio. Serve para o revestimento de espelhos, para a fabricação de corantes e de fulminato de mercúrio.

As atividades industriais e a utilização de combustíveis fosseis geralmente são acompanhadas de grandes derramamentos de mercúrio nos meios naturais. Quando um curso de água é poluído por mercúrio, parte deste se volatiliza na atmosfera e depois torna a cair em seu estado original, com as chuvas. Uma outra parte, absorvida direta ou indiretamente por plantas ou animais aquáticos, circula e se concentra em grandes quantidades ao longo das cadeias alimentares. Além disso, a atividade microbiana transforma o mercúrio metálico em compostos orgânicos de mercúrio, altamente tóxicos. É assim que se explica o forte conteúdo de tiometil-mercúrio encontrado nos peixes da baia de Minamata no Japão. No homem os efeitos químicos da intoxicação mercurial são conhecidos como hidrargirismo.

O mercúrio foi empregado na terapêutica desde a antiguidade. Atualmente ele esta sendo substituído por outros medicamentos mais potentes e menos tóxicos. Hoje ainda são usados o dicloreto de mercúrio, como anti-séptico, o monocloreto, como colagogo e purgativo, e os óxidos amarelo e vermelho, em pomadas dermatológicas e oftalmológicas. O cianeto de mercúrio foi utilizado em alguns casos de sífilis visceral e os diuréticos mercuriais estão praticamente fora de uso. O mercúrio cromo e o mercúrio butol são ainda usados como anti-sépticos em ferimentos.

O mercúrio faz parte da família do Zinco junto com o cádmio. Algumas propriedades dos três elementos estão ilustrados na tabela a seguir.

Tabela I – Algumas propriedades da família do zinco.

Propriedade	**Zn**	**Cd**	**Hg**
Número Atômica	30	48	80
Número de isótopos naturais	5	8	7
Massa atômica	65,39	112,411	200,59
Configuração eletrônica	[Ar] $3d^{10}4s^2$	[Kr] $4d^{10}5s^2$	[Xe] $4f^{14}6s^2$
Eletronegatividade	1,6	1,7	1,9
Raio do metal (pm)	134	151	151
Raio iônico efetivo (pm) II	74	95	102
I	-	-	119
Potencial de ionização kJ/mol 1°	906,1	876,5	1007
2°	1733	1631	1809
3°	3831	3644	3300
E° (M^{++}/M)/V	-0,7619	-0,4030	0,845
Ponto de fusão (°C)	419,5	320,8	-38,9
Ponto de ebulição (°C)	907	765	357
□H_{fus} (kJ/mol)	7,28	6,4	2,30
□H_{vap} (kJ/mol)	114,2	100	59,1
□$H_{gás\ monoatômico}$ (kJ/mol)	129,3	111,9	61,3
Densidade (25°C) (g/cm^3)	7,14	8,65	13,53
Resistência elétrica (20°C) (□ohm/cm)	5,8	7,5	95,8

CORROSÃO POR MERCÚRIO

O mercúrio é um elemento altamente corrosivo. Ele fragiliza ligas de alumínio, cobre, titânio, níquel, ferro e zinco.[1-9]

De acordo com fontes bem informadas, o mercúrio poderia ser usado desgastar e destruir estruturas de alumínio incluindo colunas de sustentação de edifícios, aeronaves e trocadores de calor. Aparentemente, durante a Segunda Guerra Mundial, o governo dos Estados Unidos estava muito preocupado com sabotagem dos Japoneses envolvendo as estruturas de alumínio de arranha-céus de Los Angeles e São Francisco na Califórnia.

Conforme outro relato, os Americanos durante a Segunda Guerra Mundial enviaram comandos para aplicar pastas com mercúrio em aeronaves no território da Alemanha e causar a "falha total" de aviões de combate.

Atualmente é expressamente proibido levar mercúrio a bordo de aeronaves e somente representantes de serviços metereológicos oficiais podem levar barômetros a bordo.

A Figura 1 ilustra um exemplo dos efeitos de mercúrio sobre uma coluna de alumínio. Como pode ser visto a coluna mostra uma degradação profunda, apresentando um esfarelamento drástico.

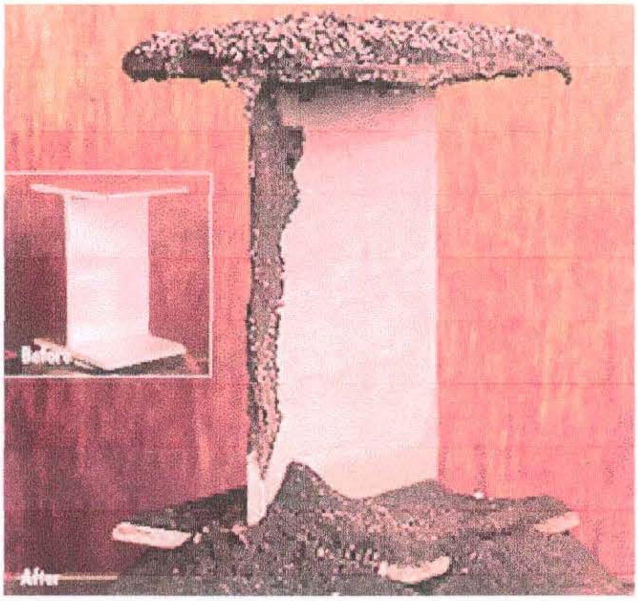

Figura 1 – Efeito corrosivo do mercúrio sobre uma coluna de alumínio.

"Liquid Metal Embrittlement" (LME) – esfarelamento por metais líquidos – é um processo complexo que fratura a estrutura de metais e acontece repentinamente, sem aviso. Há mais de quatro décadas é conhecido o efeito devastador do mercúrio sobre alumínio, e a acumulação do mercúrio em plantas de gás natural e na indústria do petróleo levou a conseqüências graves. O mesmo tipo de problema também acontece ocasionalmente em trocadores de calor na indústria petroquímica.[1-5, 7, 8, 10]

As condições necessárias para LME acontecer são as seguintes:

1) a presença de um metal líquido; dentro dos quais o mercúrio é o mais conhecido e atua mais intensamente sobre ligas de alumínio;
2) a presença de um valor limiar de tensão, que pode ser inferior a 5% do campo de tensão para algumas condições para ligas de alumínio;
3) molhamento da liga pelo metal líquido, que no caso de liga de alumínio requer a ruptura da película de óxido.

FORMA DE ATAQUE DO HG EM TROCADORES DE ALUMÍNIO

O mercúrio está presente em quantidades muito pequenas no gás natural e nas correntes de refinaria, e as vezes pode acumular em quantidades suficientes para causar e corrosão e falha em trocadores criogênicos de calor. O sistema de resfriamento, no processo de separação de gases usa um trocador de calor de placas aletadas de alumínio. Normalmente o núcleo do trocador é uma liga de alumínio 3003, com cabeçotes, admissões e tubulações de alumínio 5083 (a mais comum) ou 6061. O mercúrio degrada as caixas frias de alumínio provavelmente por três mecanismos. A Figura 2 ilustra um trocador de calor criogênico típico ilustrando as sua conexões.

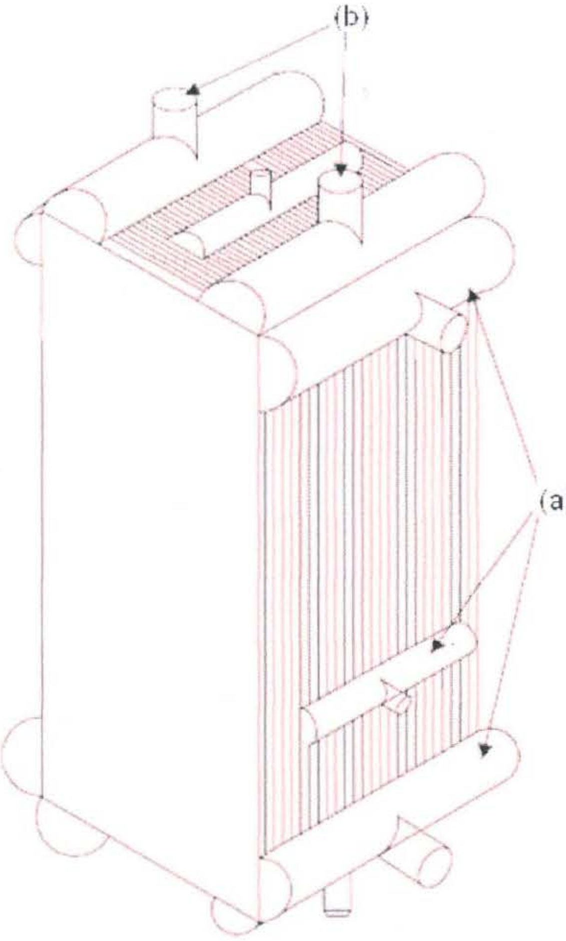

Figura 2 – Vista esquemática de um trocador de calor criogênico mostrando distribuidores (a) e bocais (b).[1]

MECANISMOS DE DEGRADAÇÃO DE ALUMÍNIO

Amalgamação

A amalgamação é um processo através do qual o mercúrio forma soluções com vários metais, incluindo Al, Au, Ag e Zn. No caso do alumínio a concentração do mesmo no amalgama é muito baixa e a profundidade do ataque é limitada. Além disso, o alumínio impede o contato direto com o mercúrio através de uma superfície protetora de óxido (Al_2O_3). A reação de amalgamação do mercúrio acontece através do molhamento da superfície metálica do alumínio. O óxido de alumínio não é homogêneo, contém muitos defeitos e o mercúrio normalmente não penetra através destes defeitos e rachaduras microscópicas para poder atingir a camada metálica subjacente. Porém, se a extensão e a severidade destes defeitos é aumentada por tensão mecânica ou térmica, abrasão ou alguma mudança química no ambiente, o risco de dano por mercúrio aumenta.

Corrosão por amalgama

A corrosão por amalgama acontece na presença de mercúrio e umidade e o processo se propaga com quantidades minúsculas de mercúrio. A reação é a seguinte:

$$Hg + Al \longrightarrow Hg(Al) \text{ amalgama}$$

$$Hg(Al) + 6H_2O \longrightarrow Al_2O_3.3H_2O + 3H_2 + Hg$$

Quantidades pequenas de alumínio podem dissolver-se no mercúrio líquido, difundir na interface mercúrio-ar úmido e subsequentemente oxidar de maneira rápida. Como o processo de oxidação retira alumínio do mercúrio, mais alumínio pode dissolver-se e este processo pode continuar até quando todo o alumínio tenha sido oxidado. Na prática, podem ser observados *whiskers* (bigodes) volumosos de óxido e *pits* (sulcos) profundos. A velocidade de oxidação depende da presença de umidade e a reação é lenta no caso de ambientes secos.

Vários pesquisadores descreveram o amalgama de Al e Hg como um produto branco, fibroso que pode ter a forma amorfa de γ-Al_2O_3, uma forma hidratada de alumina (Al_2O_3) ou hidróxido de alumínio. A presença de íons na água é necessária para a corrosão do amalgama. Aparentemente, os íons desestabilizam a camada protetora de óxido permitindo ao mercúrio entrar em contato com o metal. Não há dúvida que o mercúrio pode causar ataques catastróficos no alumínio na presença de água. Isto, porém não acontece em trocadores de calor criogênicos, onde a presença de água é extremamente rara e até agora não foi constatada em nenhum caso de falhas.[1-5, 7, 8, 9]

Esfarelamento por metal líquido (Liquid Metal Embrittlement – LME)

LME de ligas de alumínio por mercúrio é um exemplo de um processo comum onde metais líquidos esfarelam ou deterioram outros metais ou ligas. Por exemplo, o mercúrio deteriora ligas de Al, Cu, Ti, Fe e Zn. O mercúrio não afeta ligas de Mg. Por outro lado, ligas de Al são afetadas também por Ga, In, Pb, Sn, Cd e Na líquidos. Existem vários tipos de LME e com mecanismos diferentes. Na maioria dos casos, os átomos dos metais que causam a deterioração adsorvem-se em superfícies com muita tensão ou com fraturas. Este é o caso do sistema Al-Hg.

LME é um processo muito mais severo que outros tipos de fragilização como por exemplo: fragilização por hidrogênio e fratura causada em peças corroídas sob tensão. No caso do LME, uma vez que as trincas foram iniciadas acontecem muito rapidamente fraturas subcríticas até em caso de tensões muito baixas. As fraturas acontecem preferencialmente ao longo da fronteira de grãos da dupla Al:Hg, porém fraturas transgranulares podem também acontecer. Metais líquidos penetram nas fraturas crescentes. Desta maneira a ponta da trinca está sempre em contato com os átomos do metal que fragiliza. O processo que controla a velocidade de fratura está ainda em debate, porém em alguns casos, não há dúvida que a velocidade de escoamento do líquido nas trincas controla a velocidade de fratura.

A adsorção de átomos fragilizantes nas trincas debilita as ligas interatômicas do substrato e auxilia o crescimento de fraturas facilitando a ruptura ou o deslizamento das ligações interatômicas mais facilmente que no caso de ambientes inertes. Adsorção preferencial na fronteira do grão/interseções na superfície resulta preferencialmente em fraturas intergranulares.

Normalmente, os processos de fraturas em ambientes com metais líquidos exibem menor plasticidade do que no ar. Portanto, as superfícies de fratura, na presença de metal líquido, exibem pouca ou nenhuma ondulação, ao contrário das fraturas no ar onde as ondulações são profundas e grandes.

Películas finas de metal líquido ficam atrás da frente de avanço de uma fratura e conseqüentemente as superfícies fraturadas são cobertas por uma película de metal líquido. Para o sistema Al:Hg o processo de secagem (*de-wetting*) pode acontecer, de tal forma, produzindo gotículas de mercúrio nas superfícies fraturadas.

A presença de mercúrio nas mesmas pode também levar a formação de *whiskers* de óxido depois da fratura.

Para iniciação de fraturas através de LME deve existir um contato intimo entre o metal líquido e o metal sólido, sem a presença de uma película de óxido que previne o molhamento e adsorção. Todas as ligas são cobertas por uma película fina protetora de óxido e as superfícies as vezes podem ficar cobertas por mercúrio líquido por tempo indefinido sem nenhuma reação até o momento em que a película de óxido seja danificada. As películas de óxidos podem ser quebradas por processos mecânicos, riscamento ou abrasão, processo químicos, por exemplo, corrosão, ou por deformação do alumínio resultando em degraus de deslizamento na superfície. Este tipo de processo é comum em plantas de liquefação de gás natural e na indústria petroquímica.

Os trocadores de calor criogênicos são comumente fabricados com a liga Al5083 uma liga de alumínio e magnésio. O siliceto de magnésio pode contribuir para endurecer as ligas pelo envelhecimento. À temperatura ambiente o alumínio pode conter em solução aproximadamente 1% de magnésio, porém, os trocadores de calor contém 4,5%, são ligas meta estáveis que as vezes precipitam Al_3Mg_2. Este fenômeno é muito lento a temperaturas ambiente e criogênica, porém, se esta liga sofre processos de soldagem a zona termicamente atingida (ZTA) apresentam uma diminuição considerável no fator k (fator de concentração de tensões), aumentando consideravelmente a sensibilidade ao ataque por metais líquidos.

Uma caixa fria em um trocador de calor criogênico tipicamente inclui distribuidores com vários bocais. Os distribuidores e os bocais são fabricados utilizando-se junções soldadas. LME pode causar fraturas extensivas por delaminação nos distribuidores e fraturas intergranulares no campo circunferencial das soldas. As Figuras 3 (a) e 3 (b) mostram exemplos típicos de fraturas longitudinais e delaminação.

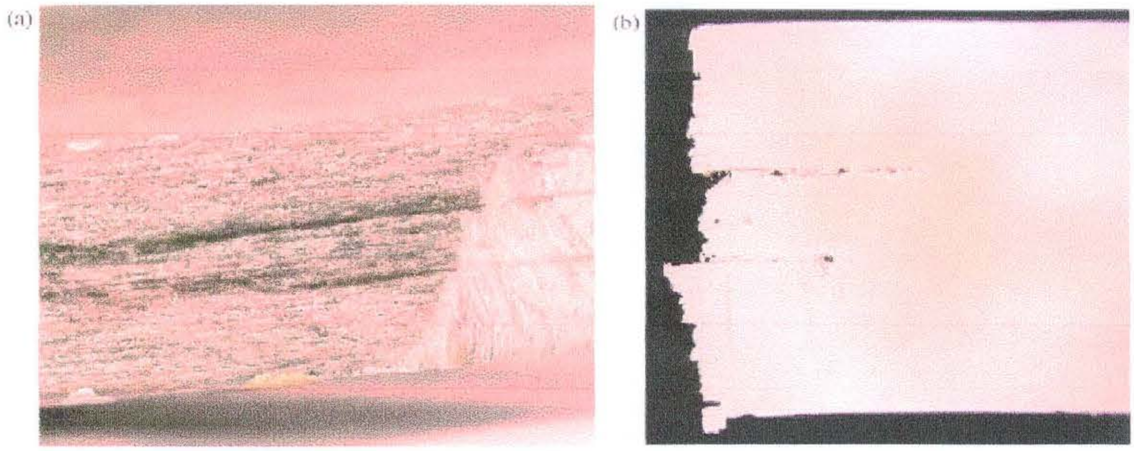

Figura 3 – (a) Fotografia mostrando a superfície da fratura longitudinal e das fraturas de delaminação. (b) secção transversal da fratura após polimento mostrando a natureza e o comprimento da trinca.[1]

Detalhes amplificados do mesmo tipo de fraturas estão ilustrados nas Figuras 4 (a) e 4 (b). Alguma das fraturas mostradas na Figura 3 atingiram profundidades de 50mm e como pode ser visto nas micrografias da Figura 4 a fratura apresentou ramificações. Mais detalhes macroscópicos estão ilustrados nas Figuras 5 e 6.

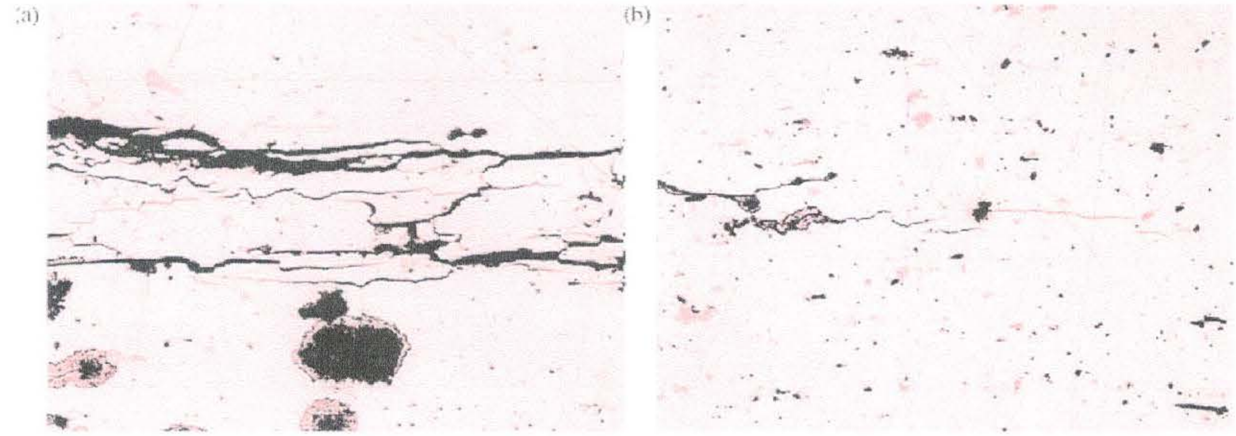

Figura 4 – Secção mostrando as múltiplas trincas próximas da superfície da fratura longitudinal (a) e próximo do fim da fratura por delaminação (b) (aumento de 165 X).[1]

Detalhes das fraturas apresentadas nas Figuras 5 e 6 são apresentadas em micrografias nas Figuras 7 (a) e 7 (b). Nelas podemos observar a fratura associada com a solda circunferencial. Estruturas granulares equiaxiais da solda são evidentes. Também podem ser observadas fraturas secundárias que tem origem na fratura inicial ou primária. O desenvolvimento da fratura acontece a partir do interior para a superfície externa.

As Figuras 8 (a) e 8 (b) ilustram micrografias que foram obtidas na área circumferencial da solda após limpar a superfície com ácido nítrico para remover os produtos de corrosão e o mercúrio contaminante. A fratura na superfície através da solda circunferencial revelou estruturas granulares e também algumas trincas intergranulares.

Vistas mais detalhadas de fraturas superficiais longitudinais em um margem elevada (patamar) mostrando fraturas adicionais através da lamela e rupturas com imagens visíveis estão ilustradas nas Figuras 9 (a) e 9 (b).

Figura 5 – Exemplos de fraturas de delaminação que desviou e cruzou a superfície interna, com *whiskers* de alumina marcando claramente as trincas.[1]

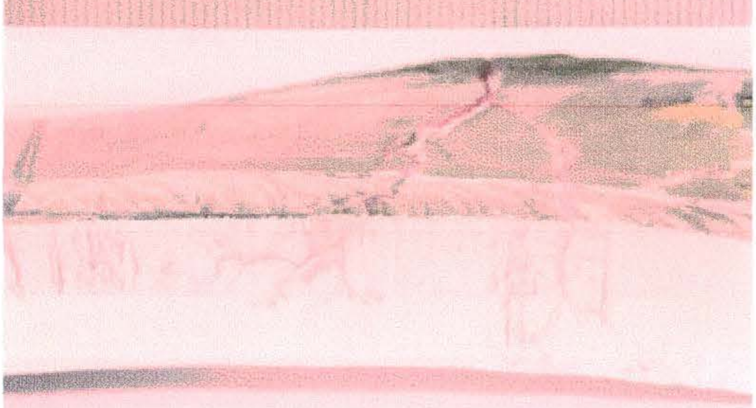

Figura 6 – Vista macroscópica de uma secção da solda cicunferencial, mostrando fratura intergranular pronunciada e ramificada.[1]

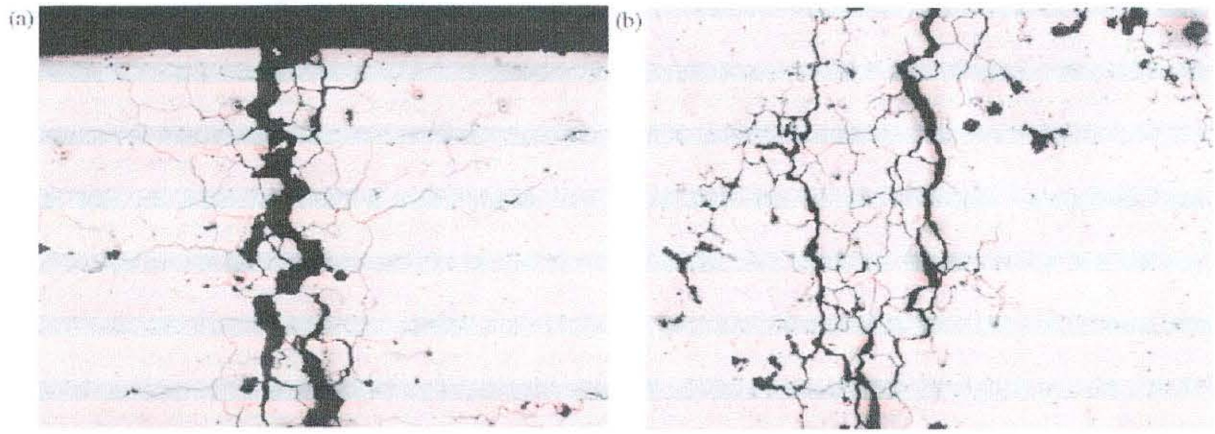

Figura 7 – Trincas na superfície externa da solda circunferencial (a) e no interior dela (b), ilustrando fratura intergranular ramificada (aumento de 141X). [1]

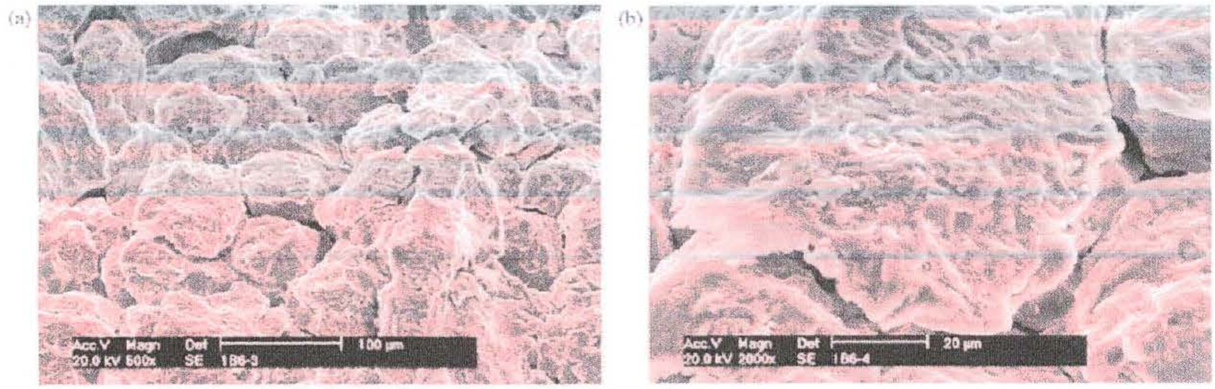

Figura 8 – Superfície de fratura na solda circunferencial, mostrando a natureza intergranular e ramificada das trincas. [1]

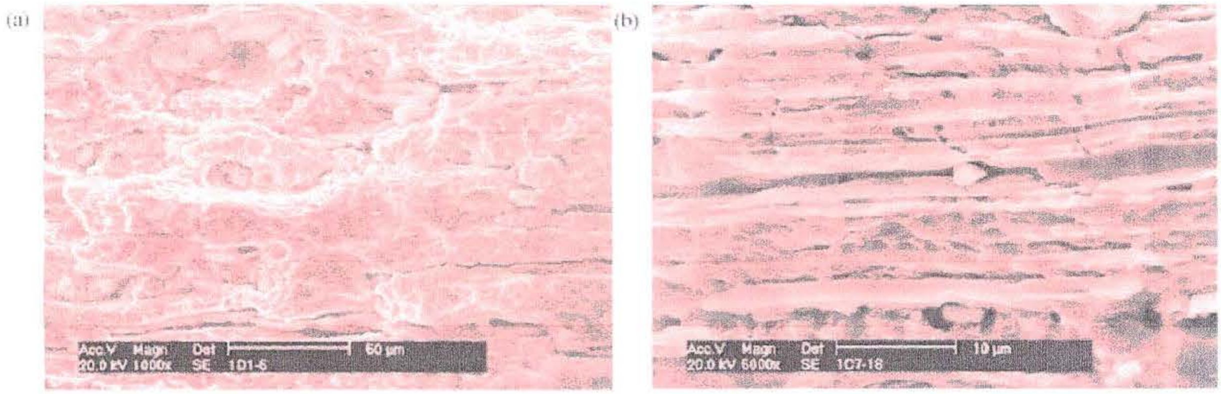

Figura 9 – (a) Superfície de fratura longitudinal no topo de margem elevada e (b) ilustrando fratura lamelar. [1]

O processo LME fratura ligas de alumínio por mercúrio e requer a presença de mercúrio no estado líquido, tensão acima do valor limiar que pode ser abaixo de 5% para a liga de Al5083-0 e molhamento da superfície do material pelo metal líquido. O molhamente requer a ruptura da película de óxido entre o substrato e o metal líquido as superfícies fraturadas sempre mostravam a presença de gotas de mercúrio, associadas com a formação de *whiskers* de óxido de alumínio. Estas duas características, quando observadas em superfícies fraturadas indicam LME como mecanismo de falha.

Em plantas de processamento de gás natural e na petroquímica, quantidades consideráveis de mercúrio podem ser coletadas nos trocadores de calor criogênicos. As quantidades substanciais de mercúrio (quilos por ano) tem a sua origem em traços de mercúrio no gás natural e no petróleo. O mercúrio condensa e acumula nas partes de resfriamento do sistema se não é removido na entrada. Tipicamente o mercúrio condensa nas superfícies na forma sólida a temperaturas inferiores a -39 C°. Este mercúrio sólido funde formando mercúrio líquido que acumula nas partes baixas das tubulações e bocais dos sistema do trocador de calor quando a planta é parada.

Sem dúvida alguma as altas tensões próximas as regiões soldadas e a tendência do mercúrio acumular-se nos rebaixos deixados pela solda, indicam que na maioria das vezes o ponto de iniciação da LME é nas soldas.

Uma vez iniciadas as fraturas na liga Al5083-0 elas crescem muito rápido (até dezenas de milímetros por segundo). Existe uma grande variação no tempo de iniciação de fraturas e isso explica porque as vezes alguns bocais são altamente danificados e outros paralelos, apesar de ter mercúrio, não exibem fraturas. É justamente por isto que é muito difícil a inspeção e prevenção de fraturas induzidas por LME. Por exemplo, a detecção de fraturas por ultrasom requer que a planta seja parada. Radiografia pode localizar os pontos onde o mercúrio acumulou e permitir a remoção do mesmo e a inspeção destas regiões. A desvantagem é que uma vez as trincas foram infiltradas por mercúrio a falha é eminente.[1,6,8]

Entre outras coisas, a extensão e a quantidade de fraturas depende da quantidade de mercúrio presente na matéria prima. Obviamente a remoção do mercúrio na entrada diminui a probabilidade de falha nos trocadores de calor.

Mercúrio líquido em contato com o alumínio pode causar falhas rápidas e sérias. Mercúrio, presente até em quantidades muito pequenas no gás natural e no petróleo, pode ser concentrado em sistemas de destilação criogênica. Se o mercúrio está presente na forma líquida (por exemplo durante períodos de interrupção ou paradas das plantas), ele pode causar danos catastróficas em trocadores de calor de alumínio. As fraturas podem acontecer sem aviso e por causa do crescimento rápido das mesmas através do LME não existe nenhuma técnica adequada e não-destrutiva para monitorar e proteger as instalações.

REFERÊNCIAS

1. R. Coade and D. Coldham, *International Journal of Pressure Vessels and Piping, 83*, 336-343 (2006).
2. S. Coleman, J. Ries, D. Campbell and K.R. Clark, "Mercury Removal from Cracked Gas and Liquid Streams", presented at 2005 AIChE Spring National Meeting, 17th Annual Ethylene Producers' Conference, Session TA009 – Ethylene Plant Operations, Atlanta, GA, April 12, 2005.
3. T.Y. Yan, *Ind. Eng. Chem., 33*,3010-3014 (1994).
4. S. Mark Wilhelm and N. Bloom, *Fuel Processing Technology, 63*, 1-27 (2006).
5. Z. Spiric, "Innovative Approach to the Mercury Control During Natural Gas Processing", Proceedings of ETCE 2001, Engineering Technology Conference on Energy, February 5-7, 2001, Houston Texas, USA.
6. S. J. Pawel, J.R. DiStefano and E.T. Manneschmidt, "Effect of Surface Conditions and Heat Treatment on Corrosion of Type 316L Stainless Steel in A Mercury Thermal Convection Loop", ORNL/TM-2001/195, Report Prepared for the U.S. Department of Energy, Oak Ridge National Laboratory, Oak Ridge Tennessee, 2001.
7. J. S. Thompson and J. H. Pavlish, *Fuel Processing Technology, 65-6*,167-175 (2000).
8. K. Ina and H. Koizumi, *Materials Science and Engineering",A387-389*, 390-394 (2004).
9. Y.B. Xu, Y. Zhang, Z.G. Wang and Z.Q. Hu, *Scripta Metallurgica et Materialia, 33(2)*, 179-183 (1995).
10. , K. Crippen and S. Chao, "Mercury in Natural Gas and Current Measurement Technology" 1997 Gas Quality and Energy Measurement Symposium, February 3-5, Orlando, Florida, pp. 1-16.

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GLIMPSES OF THE HISTORY OF CHEMISTRY IN MEXICO

Lavinel G. Ionescu* [a, b] and Luis Alcides B. De Boni[c]

[a]Scienco Scientific Consulting Services
Viamão, Rio Grande do Sul, BRASIL

[b]Sarmisegetusa Research Group
Santa Fe, New Mexico, USA

[c]Tchê Química Ltda.
Porto Alegre, Rio Grande do Sul, BRASIL

ABSTRACT

The present article describes some aspects of the history of chemistry in Mexico. Some developments of interest of the Pre-Hispanic or Pre-Columbian Period are treated briefly. For the Colonial Period, the importance of the School of Mines of Mexico City, the discovery of vanadium and other contributions of Andrés Manuel Del Rio are discussed in detail. For more recent times, the work of Xorge Alejandro Dominguez in the area of natural products and the study of the ozone layer by Mario José Molina, Nobel Prize in Chemistry, are presented.

RESUMO

O presente artigo descreve alguns aspectos da história da química no México. Alguns desenvolvimentos interessantes do Período Pré-Hispânico ou Pré-Colombiano são mencionados de maneira sucinta. Para o período Colonial, são discutidos em detalhe a importância da Escola de Minas da Cidade do México, a descoberta do vanádio e outras contribuições de Andrés Manuel Del Rio. Para tempos mais recentes, as contribuições de Xorge Alejandro Dominguez na área de produtos naturais e de Mario José Molina, Prêmio Nobel em Química, ao estudo da camada de ozônio são tratados em detalhe.

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a *To whom correspondence should be addressed at:
lavinel@ibest.com.br
lavinel@pop.com.br

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INTRODUCTION

Contrary to general belief in certain circles, many scientists that were born, lived or worked in Latin America, made important contributions to chemistry. Among them are Bartolomé de Medina who set up amalgamation as an industrial process in 1555 in Zacatecas, México; Carlos Siguenza y Góngora, Mexican astronomer and cosmographer, known especially for his studies of comets; Antonio de Ulloa, who was the first to take platinum to Europe; Fausto and Juan José Delhuyar, discoverers of tungsten; Andrés Manuel del Rio, discoverer of vanadium; José Caldas, Director of the Observatory of Bogotá, Nueva Granada (Colombia), who studied the variation of the boiling point of water with altitude and is better known for contributions in astronomy, mathematics and botany; José Luis Casaseca, founder of the Cuban Institute of Chemical Research in 1848; Alvaro Reynoso, father of modern sugar technology and Luis Frederico Leloir, Nobel Laureate in Chemistry. Significant contributions were also made by Horácio Damianovich in noble gas chemistry, Gustavo Fester, Xorge Alejandro Dominguez and Otto Gottlieb in natural products and Ernesto Giesbrecht in the chemistry of lanthanides.[1-28] In 1995 the Mexican Chemist Mario José Molina was awarded the Nobel Prize in Chemistry together with Paul Crutzen and F. Sherwood Rowland for their work on the ozone layer.

The history of Mexico is generally subdivided into four large periods. They are the following:

1. Prehistoric and Pre-Hispanic Period (Beginning -1517).
2. Period of Conquest and Colonization by the Spanish (1517-1810)
3. Period of the Struggle for the Independence and the Establishment of the Mexican State (1810-1910).
4. Period of Modern Mexico (1910-Present).

The present article presents some glimpses of the history of Chemistry in Mexico.

PRE-HISPANIC OR PRE-COLUMBIAN PERIOD

According to some, Latin America was and still is a scientific desert and and there was no such thing as Pre-Hispanic or Pre-Columbian science.[18] Nobody however can deny the existence of vast empirical knowledge in astronomy, agriculture, civil engineering, metallurgy, medicine, the art of embalming, and the chemistry of medicinal plants and dyes. Did the building of the pyramids, the calendaristics of the Aztecs and Mayas and the development of agriculture, water supply, irrigation and medicine, especially by the Incas, involve science?

AZTEC CALENDAR, SYMBOL OF PERIODIC ONDULATORY BEHAVIOR THE UNIVERSE AND TOKEN OF THE ETERNITY OF KNOWLEDGE.

THE AMAZING EQUINOX NATURAL SPECTACLE: THE SERPENT COMING DOWN THE PYRAMID. CHICHEN-ITZÁ, YUCATÁN, MEXICO.

At least seven metals, among them iron, gold, copper, lead, silver and tin were used in the Pre-Columbian Period. When Ferdinand Cortez asked the Aztecs from where they obtained their knives, they pointed to the sky (meteoritic iron of celestial origin). The Incas developed sophisticated smelting and alloying processes and their blast furnaces used the wind from the Andes. [19-28]

The use of medicinal plants by the Aztecs is well-documented and will be mentioned only in passing. Soon after the Conquest, many Spanish explorers and physicians spent years studying Aztec medicine. For details, we cite especially the work of Bernardo Ortiz de Montellano that spans more than three decades. [23,29]

Today there is vast interest in folk and traditional remedies throughout the world and the subject is treated by a new branch of science called ethnopharmacology.[30,31]

COLONIAL PERIOD

The Colonial Period is characterized by numerous scientific expeditions studying relief, fauna, flora, population and natural resources.

The Spanish founded more than thirty (30) universities and institutions of higher learning in the New World. The first university founded was the University of Santo Domingo (1535), followed by the University of Mexico (1551) and San Marcos, Lima (1551). We also mention the Colegio del Rosario, Bogotá, Colombia (1580), Colegio de Cordoba, Argentina (1613) and the University of Havana (1722). The Colegio de Minería of Mexico City was established in 1792 and the Cuban Institute of Chemical Research in 1848.

CATHEDRAL OF MEXICO.

Of course, the main motivation of all this scientific activity was the maximum exploration of all the resources available in the New World.[11-22]

For example, Francisco Fernandez, Medico de Camara at the Court of Philip II went to Mexico in 1570 and spent seven years studying Aztec medicine and medicinal plants. Notable contributions were made in all areas of science beginning with astronomy, cosmography and cartography and including agriculture, animal husbandry, botany, medicine, metallurgy and others.

José Celestino Mutis (1732-1808), Spanish physician and botanist, investigated the chincona forests of Colombia and collaborated with Juan José de Elhuyar in various aspects of mining.

Antonio de Ulloa, member of a distinguished Spanish family, was born in 1716 and died in 1795.He studied physics and mathematics and was a member of many scientific societies, including the Academy of Sciences of Paris and the Royal Society of London. He traveled widely in Europe and the Americas and occupied many important positions, including those of Frigate Captain, Commander of the Royal Squadron of the Spanish Armada, Governor of Huancavélica-Peru, Florida and Louisiana.[14,32]

In 1735, while a member of a scientific expedition sent by the Spanish and French governments to South America to measure the degree of meridian in Quito, close to the equator, he discovered platinum in the mines of Lavadero or wash gold in the district of Chocó, in the western part of present day Colombia.[14,32-36]

From the point of view of chemistry, the most important development is probably the establishment of the school of mines in Mexico and Colombia (Colegio de Minería, Mexico and Colegio del Rosario, in Santa Fe de Bogotá, Colombia).

The Delhuyar (de Elhuyar, D'Elhuyar) brothers Fausto and Juan José played a very important role. They traveled in many parts of Europe, studied and worked at the Seminary of Vergara where they discovered tungsten or wolfram in 1783.

POSTAGE STAMP FROM SPAIN COMEMORATING 200 YEARS FROM THE DISCOVERY OF TUNGSTEN OR WOLFRAM BY THE DELHUYAR BROTHERS

The older brother Juan José (1754-1796) went to Colombia in 1786, where among other things he founded the School of Mines of the Colegio del Rosario in Bogotá. He died in Colombia and members of his family are national heroes of the war of independence from Spain.

Fausto Delhuyar (1755-1833) spent more than 30 years in Mexico and upon his return to Spain occupied many important positions.

In 1788, by Royal Edict, Fausto de Elhuyar was appointed Director General of the Royal Assembly of Mines of Mexico. Soon after his arrival in Mexico City he supervised the construction of a chemical laboratory and assay furnaces.

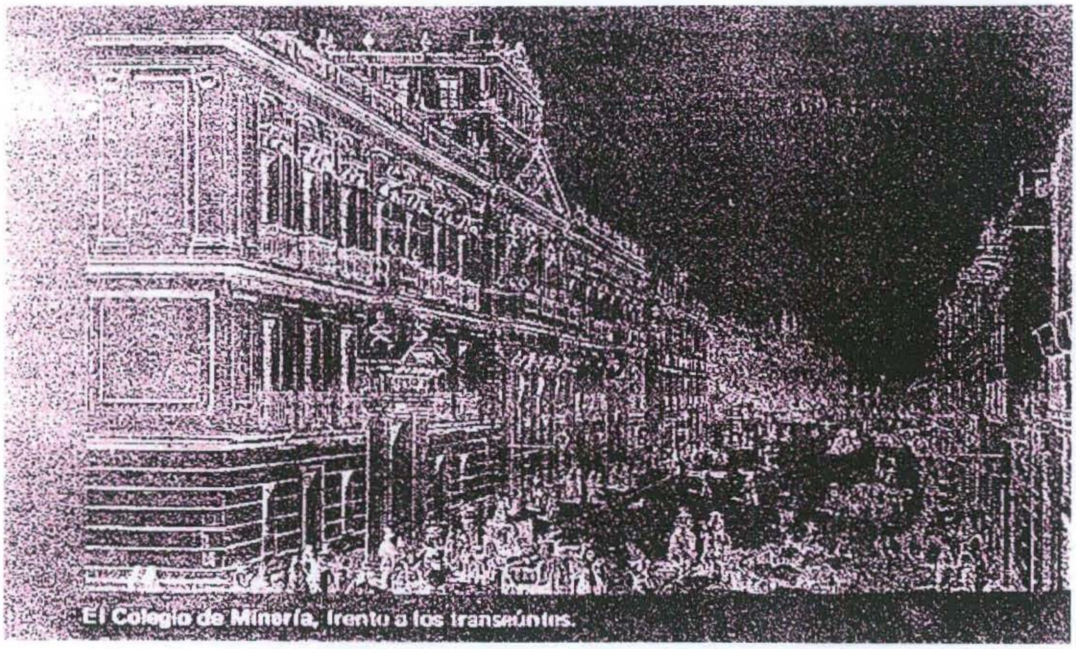
Elhuyar en Viena, 1788.

FAUSTO DE ELHUYAR (1755-1833)
DISVOVERER OF TUNGSTEN AND FOUNDER OF THE SCHOOL OF MINES OF MEXICO

JUAN JOSÉ DE ELHUYAR (1754-179)
DISCOVERER OF TUNGSTEN AND FOUNDER OF THE SCHOOL OF MINES OF BOGOTÁ, COLOMBIA

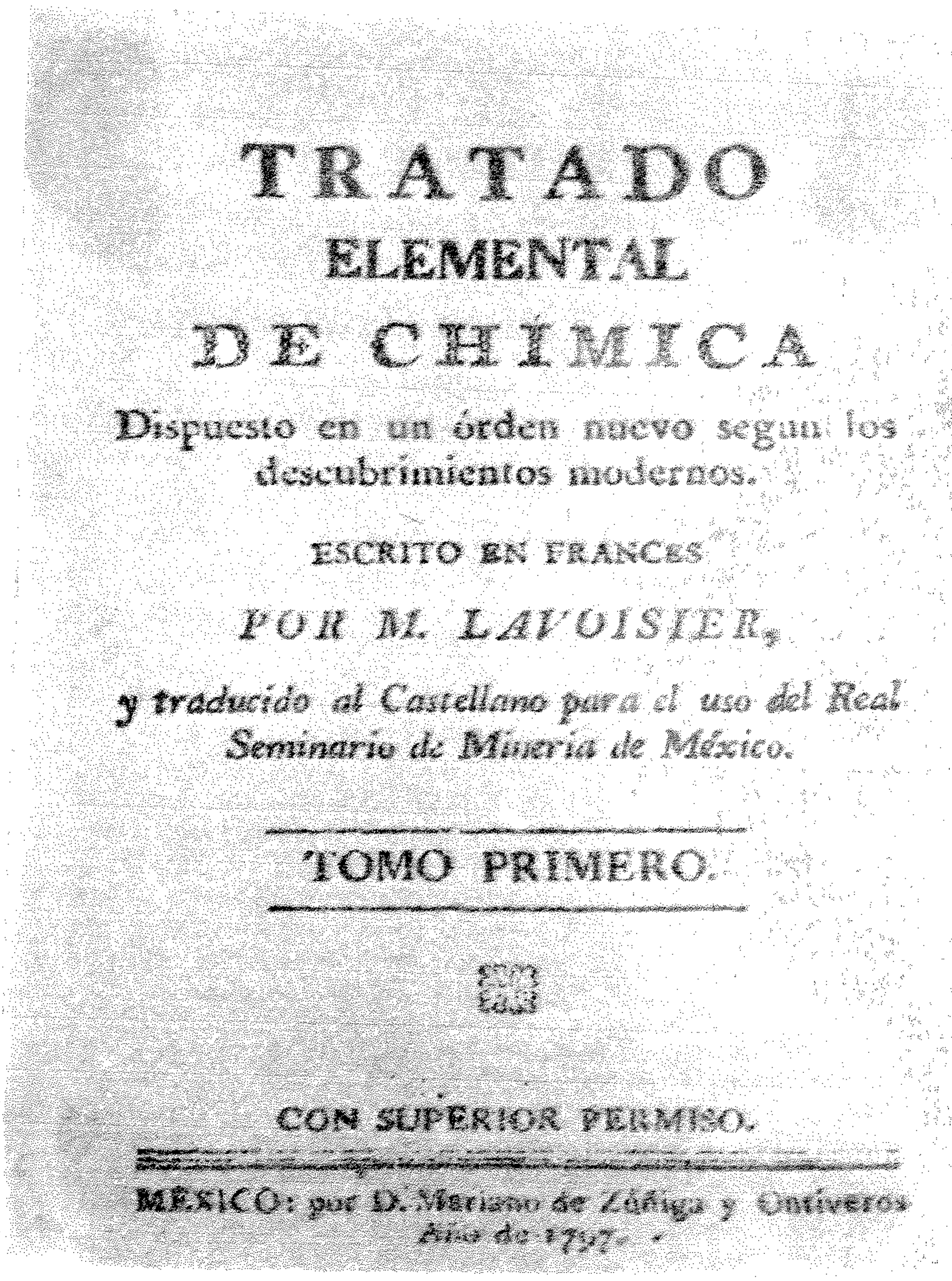
The Colegio de Mineria became a very respectable institution and during the time of Fausto de Elhuyar and Andrés Manuel del Rio was one of the best of its kind in the whole world.

Alexander von Humboldt, during his visit to Mexico, was impressed by the high quality of instruction and research done at the School of Mines, especially by Fausto de Elhuyar and Andrés Manuel del Rio.[14,37,38]



THE SCHOOL OF MINES OF MEXICO FROM AN ENGRAVING OF THE TIME

The first Spanish translation of Lavoisier's "*Traité Elementaire de Chimie*" was published in Mexico City in 1797 and used at the School of Mines.



TRATADO
ELEMENTAL
DE CHÍMICA
Dispuesto en un órden nuevo segun los
descubrimientos modernos.

ESCRITO EN FRANCES
POR M. LAVOISIER,
y traducido al Castellano para el uso del Real
Seminario de Minería de México.

TOMO PRIMERO.

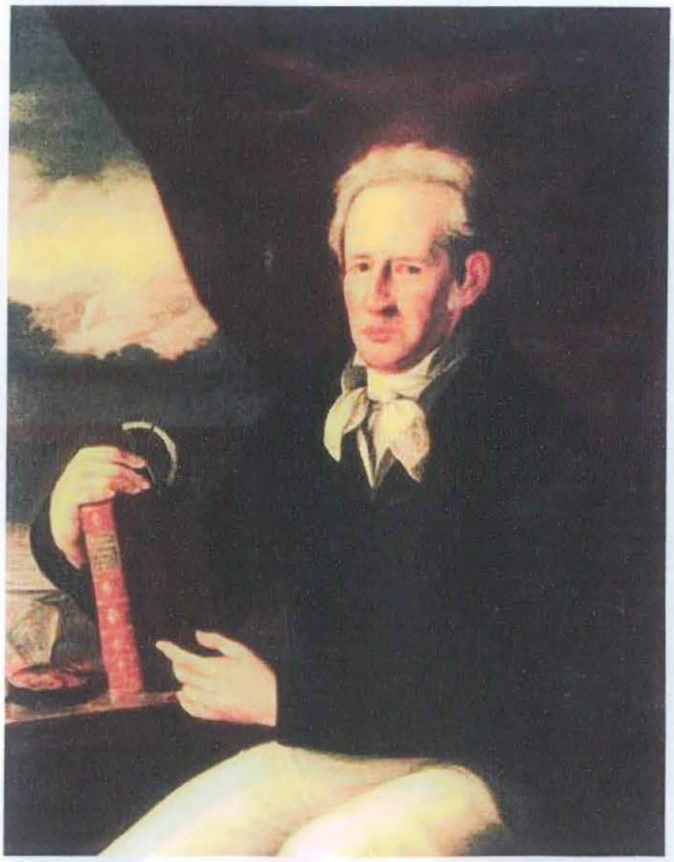
CON SUPERIOR PERMISO.

MEXICO: por D. Mariano de Zúñiga y Ontiveros
Año de 1797.

ANDRÉS MANUEL DEL RIO, DISCOVERER OF VANADIUM

Andrés Manuel Del Rio was born in Madrid on November 10, 1764 and passed away in Mexico City on March 23, 1849. He studied mineralogy, geology, metallurgy and mining engineering at the Royal Academy of Mines of Almadén and the Patriotic Seminary of Vergara. It was at the School of Mines of Vergara that Fausto and Juan José Delhuyar discovered tungsten or wolfram in 1783.

After completing studies in Spain, Del Rio received a stipend from the Spanish Crown and in 1781 traveled to Paris and later to Freiberg, Chemnitz (Schemnitz) and other scientific centers throughout Europe. He returned to Spain more than a decade later, in 1793. In Paris, he studied chemistry with Darcet and acquired experience in porcelain and ceramics manufacturing and processing. In Chemnitz, Freiberg and various metallurgic centers in France, England and other European countries, Del Rio specialized in metallurgy and mining engineering. While in Freiberg, he was a devoted student of Abraham Gottlob Werner and became fascinated by mineralogy.[38]



**ANDRÉS MANUEL DEL RIO (1764-1849)
DIRECTOR OF THE SCHOOL OF MINES OF MEXICO
AND DISCOVERER OF VANADIUM.**

Soon after his return to Spain, at the invitation of Don Fausto Delhuyar, Andrés Manuel Del Rio went to Mexico City where he was appointed professor at the School of Mines (*Colegio de Minería*). He arrived in Mexico on December 18, 1794. There he lived and worked, with few interruptions, for almost half a century, until his death in 1849.

From 1820 to 1823 he represented Mexico as a deputy in the Spanish Cortes and from 1829 to 1832 he lived in exile in Philadelphia, United States. In 1820 he pleaded for Mexico's independence in the Cortes and in 1829, when the Mexican Government expelled the Spanish (although he was not included among them), he went to exile in Philadelphia, in solidarity with his fellow countrymen.

At the Colegio de Minería (School of Mines), Del Rio taught mineralogy, French, geology, mining engineering and metallurgy. He wrote nany textbooks, including *Artes de las Minas, Geometria Subterranea, Tratado de Vetas* (Treatise on Lodes or Mineral Veins) and *Elementos de Orictognosia* (Elements of Fossil Science and Mineralogy). He also translated various manuals, including the *New Mineral System of Berzelius, Textbook of Geology*, extracted from *Lethae Geognosticas* by Bronn and annotated, translated and commented Karsten'a Mineralogical Tables (*Tablas Mineralogicas de Karsten).*

Elementos de Orictognosia, by far the most important work, was first published in two volumes in Mexico in 1795 and 1805. The second expanded edition was divided in two parts, practical and theoretical. The practical part, that Del Rio considered more important and included the description of many minerals from Mexico was published in Philadelphia in 1832, during his exile in the United States. The second or theoretical part was published after his return to Mexico and a thorough revision in 1846. Alexander von Humboldt said that it was the best book on mineralogy in Spanish and Guyton de Morveau considered it the best book on mineralogy in all languages.[37,38]

On the more practical side, Del Rio developed a pump for draining water from mines, was the manager of the first formal iron and steel foundry of Latin America in Coalcomán, Michoacán, Mexico from 1805 to 1809, director of the Casa de Moneda (Public Mint), deputy in the Mining Tribunal and honorary councilman of Mexico City.

His main research interest was the study of minerals found in Mexico and in particular of vanadite , $PbCl_2.3Pb_3(VO_4)_2$. He published a large number of papers dealing with minerals and geology in the main European journals and also in scientific periodicals from Mexico and the United States.

It was in 1801, while analyzing the grey lead mineral vanadite from Zimpán, Hidalgo, Mexico that Andrés Manuel Del Rio discovered a new element that he first called *panchromium*, because of the many colors of its oxides and later *erythronium*, because of the characteristic red colors of its salts.[14,38,39]

On September 26, 1802 he communicated his discovery to Don Antonio Cabanilles (Cavanilles), who published it in the *Anales de Ciencias Naturales de*

Madrid in May of 1803 (Volume VI, Number 16). The discovery, as described by Del Rio himself in a footnote on page 6 of *Tablas Mineralogicas de Karsten* published in 1804 can be seen elsewhere. The subsequent controversy about who was really the discovere of vanadium has been treated in detail and it will not be discussed here.[14,38-42]

It is interesting to read the correspondence between Berzelius and Wöhler and the latter's lines to Liebig. They offer some astonishing clues about the side scenes and the development of science.[43]

Be it as it may, the discovery of vanadium can be considered an outstanding accomplishment for science in Mexico and Latin America. The next discovery of an element in a laboratory of the United States took place almost one and a quarter of a century later.

Andrés Manuel Del Rio' more than fifty years of service to science and to Mexico has been duly recognized. The highest prize awarded by the Chemical Society of Mexico bears his name.

PERIOD OF THE STRUGGLE FOR INDEPENDENCE AND THE ESTABLISHMENT OF THE MEXICAN STATE

For this turbulent period in the history of Mexico, we mention more as a curiosity, the contribution of two personalities, Ilarie Mitrea and Vicente de Ortigosa.[15,16,26]

Ilarie Mitrea was born in Rasinari near Sibiu, Transylvania, Romania in 1842. He was the son of a priest and studied medicine at the University of Vienna. He is one of the most interesting and erudite figures among the Romanian scholars of the nineteenth century. In addition to his profession as a physician, he was a passionate historian, anthropologist, archaeologist, ethnographer, linguist, naturalist and explorer and traveler of four continents. He counted among his friends persons like Titu Maiorescu, the notable literary critic and politician and Grigore Antipa, the famous Romanian biologist.[15]

Mitrea enrolled in the Austrian-Mexican Army after graduating from Medical School and went to Mexico in 1866. He stayed in Mexico for about two years. During this time he learned Spanish and Nahuátl (the language of the Aztecs) and in addition to performing his duties as an officer and physician in the Austrian-Mexican Army, he traveled extensively throughout Mexico, studied in depth various aspects of Mexican society and life and became a friend and helped the revolutionaries of Benito Juarez. Mitrea spent a long time in the region of Tabasco where he collected old pottery, weapons and many other artifacts that he later took to Europe. It appears that he also spent some time studying the culture of the Maya Indians near Palenque.

ILARIE MITREA (1842-1904)
ROMANIAN PHYSICIAN, NATURALIST AND EXPLORER OF FOUR CONTINENTS

Of considerable interest are Ilarie Mitrea's studies and observations concerning social and medical aspects of the Indians and Mestizos of Mexico. As a physician in a country ravaged by war, he had ample opportunity to do many comparative studies of the varying effects, morbidity and resistance to different illnesses by the local Mexican and Indian population and the European soldiers. He concluded, for example, that the Mexican and Indian soldiers were much less susceptible to septicemia (blood poisoning) than the Austrians.[15]

Like most of the other Romanians that took part in the installation of Maximilian as emperor of Mexico, Mitrea was not too convinced about the equity of the French and Austrian cause and when the opportunity arose, he helped the revolutionaries of Benito Juarez. On one occasion, in a cave near the town of San Diego, not far from Mexico City, Mitrea worked continuously for sixteen hours performing surgery on the wounded soldiers of Benito Juarez.

Ilarie Mitrea returned to Europe in April of 1867, two months before the tragic execution of Maximilian by the Mexican revolutionaries in Queretaro. He published many of his impressions, reminiscences and studies from his stay in Mexico in the Romanian review Albina (The Bee) of Vienna. In 1869, he joined the Dutch Army as a physician and traveled to Indonesia, where he spent more than twenty years working as a physician on the Island of Borneo and doing natural studies and explorations. Many of his collections of a variety of artifacts, weapons, insects, animals, minerals and medicinal plants, never seen by other Europeans are still found today in the Ethnographic Museum of Vienna, Austria , the National Museum of Bucharest and the Museum of Giurgiu in Romania.

The Mexican chemist, Vicente de Ortigosa was probably the first scientist of the American Continent to obtain a doctoral degree in chemistry. He studied with Justus von Liebig in Germany at the University of Giessen. He was awarded the doctorate in 1842 and his research studies involved the formula and structure of nicotine. [16]

PERIOD OF MODERN MEXICO

During this period that spans the last and the present centuries two developments may be considered very important.

One is the development of the petrochemical industry (PEMEX) after the expropriation and nationalization of oil reserves in 1936.

The other is the identification of steroidal components in native Mexican plants that eventually led to the establishment of SYNTEX and a strong pharmaceutical industry that was the first world wide producer of steroidal materials such as progesterone, testosterone, estradiol and cortisone.

The industrial development, especially in these two areas resulted in a high demand for trained chemists and led to a substantial increase in chemical education and research. We cite particularly the Escuela Nacional de Quimica established in 1916 and the Facultad de Quimica of the National Autonomous University of Mexico – UNAM. [16,17,22,26]

We decided to describe and treat in detail the contributions of Xorge Alejandro Dominguez, Mexico's foremost organic chemist and Mario José Molina , 1995 Nobel Laureate in Chemistry.

MEXICO CITY. CRISTOPHER COLUMBUS SQUARE AND LA REFORMA BOULEVARD.

XORGE ALEJANDRO DOMINGUEZ, MEXICO'S FOREMOST ORGANIC CHEMIST

Xorge Alejandro Dominguez, Mexico foremost organic chemist was born in Orizaba, State of Veracruz, Mexico on November 12, 1926 and died of heart attack in Mexico Cityon May 26, 1991, only hours after he had been awarded by President Carlos Salinas de Gortari the *Lázaro Cárdenas Medal* for his contributions and dedication to the scientific advancement of Mexico.[8]

He attended primary and secondary school in his native city (*Escuela Primaria Cantonal* and *Escuela Secundaria Federal Obrera de Orizaba*). He continued his studies in Mexico City and obtained the Bachelor of Science Degree in Biological Chemistry from the Instituto Politécnico Nacional in 1950. In 1952 he obtained the Master of Science Degree from Harvard University and in 1964 he was awarded the Ph.D. Degree in Chemistry by the University of Texas. In 1970, Professor X.A. Dominguez received an Honorary Doctoral Degree from the Universidad Autónoma de Guadalajara.

PROF. X.A. DOMINGUEZ (1926-1991)
MEXICO'S FOREMOST ORGANIC CHEMIST

His first faculty appointment (1946-47) was in the National School of Biological Sciences of the National Polytechnic Institute in Mexico City. From 1948 until his death, he was Professor of Chemistry at the Instituto Tecnologico y de Estudios Superiores de Monterrey – ITESM, in Monterrey, Nuevo León, Mexico. From 1957 to 1991 he acted as Chairman of the Chemistry Department of ITESM. Prof. Dr. X.A. Dominguez was Visiting Professor at many universities in different countries, including Mexico, United States, Costa Rica, Guatemala, El Salvador, Nicaragua, Colombia and Argentina. [8]

Professor X.A. Dominguez had research interests that dealt mainly with the chemistry of natural products. He discovered, isolated and identified many new chemical substances from Mexican plants and organized many international symposia and conferences dealing with phytochemistry. He has published over 250 articles and several books dealing with this subject. During the 44 year period as professor and researcher at the Instituto Tecnologico y de Estudios Superiores de Monterrey, ITESM, he acted as research advisor of more than 200 students at the graduate and undergraduate levels. More than 100 graduate students completed their master's theses or doctoral dissertations under his supervision. [8]

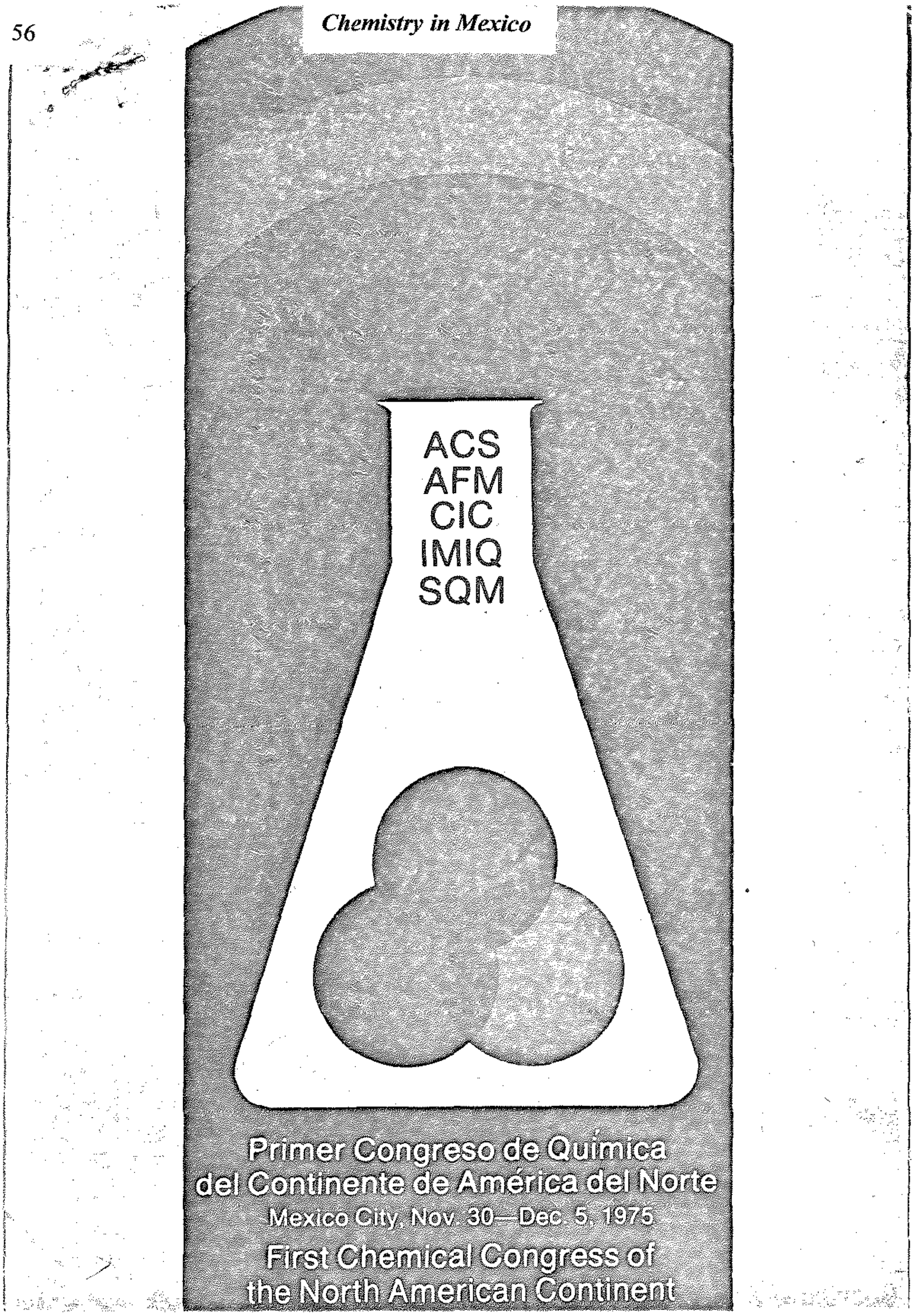
We (LGI) first met Prof. Dr. Xorge A. Dominguez in December of 1975 during the *First Chemical Congress of the North American Continent* in Mexico City. At the time he was already one of the most respected chemists in Mexico. Wherever he went, he was the center of attention, appreciation and esteem.

It is interesting to note that the *First Chemical Congress of the North American Continent* sponsored jointly by the American Chemical Society, Mexican Pharmaceutical Society, Chemical Institute of Canada, Mexican Institute of Chemical Engineering and the Mexican Chemical Society, of all cities of North America, took place in Mexico City and occurred more than a hundred years later after similar events in Europe.

Professor Xorge A. Dominguez was a very educated and erudite man, a scientist aware of his social responsibility and a patriot. He firmly believed that the main purpose of a true scientist was the search for truth and its application to the improvement of conditions of man. He was also a great educator. Like all good teachers, he believed in the power of example and thought that a teacher can teach the most by his example.[8]

According to many of his students and collaborators, who used to call him "Doctor", Prof. X.A. Dominguez was not only a professor, educator, chairman, co-worker, researcher, but also a guide , source of inspiration and example, father, friend and a lot more. Many recollect their peripatetic walks with him on the various floors of the Chemistry Building, then to the Post Office, Administration Building, Library of ITESM, etc. and back to his office. During these journeys or peregrinations with him they learned about a lot of things while accompanying the teacher. The knowledge gained could be philosophy, chemistry, politics, a new chapter of the history of Mexico, world history or about the poverty oath of the true scientist. Sometimes he would tell a lot of jokes. His office was a true "Temple of Entropy": mountains of books, journals, articles, papers and all kind of other things (cosas). There, almost in a strike of magic , he also found what he was looking for. [8]

Professor Xorge A. Dominguez was preoccupied with the teaching of science at all levels. He was the author of more than 35 chemistry books aimed for secondary school and university instruction. Among them we cite Fundamentos y Problemas de Quimica Orgánica, Limusa-Wiley, 1970; Fitoquimica, Limusa-Wiley, 1975; Quimica Orgánica Fundamental, Limusa 1980; Quimica Orgánica Experimental, Limusa 1982 and Cromatografia en Papel y Capa Delgada, OEA, Washington, 1975. He also translated about a dozen books dealing with chemistry or other areas of science, mainly from English.



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Chemistry in Mexico

ACS
AFM
CIC
IMIQ
SQM

Primer Congreso de Química
del Continente de América del Norte
Mexico City, Nov. 30—Dec. 5, 1975
First Chemical Congress of
the North American Continent

COVER PAGE OF THE PROGRAM OF THE FIRST CHEMICAL CONGRESS OF THE NORTH AMERICAN CONTINENT
Mexico City, Nov. 30 – Dec. 5, 1975.

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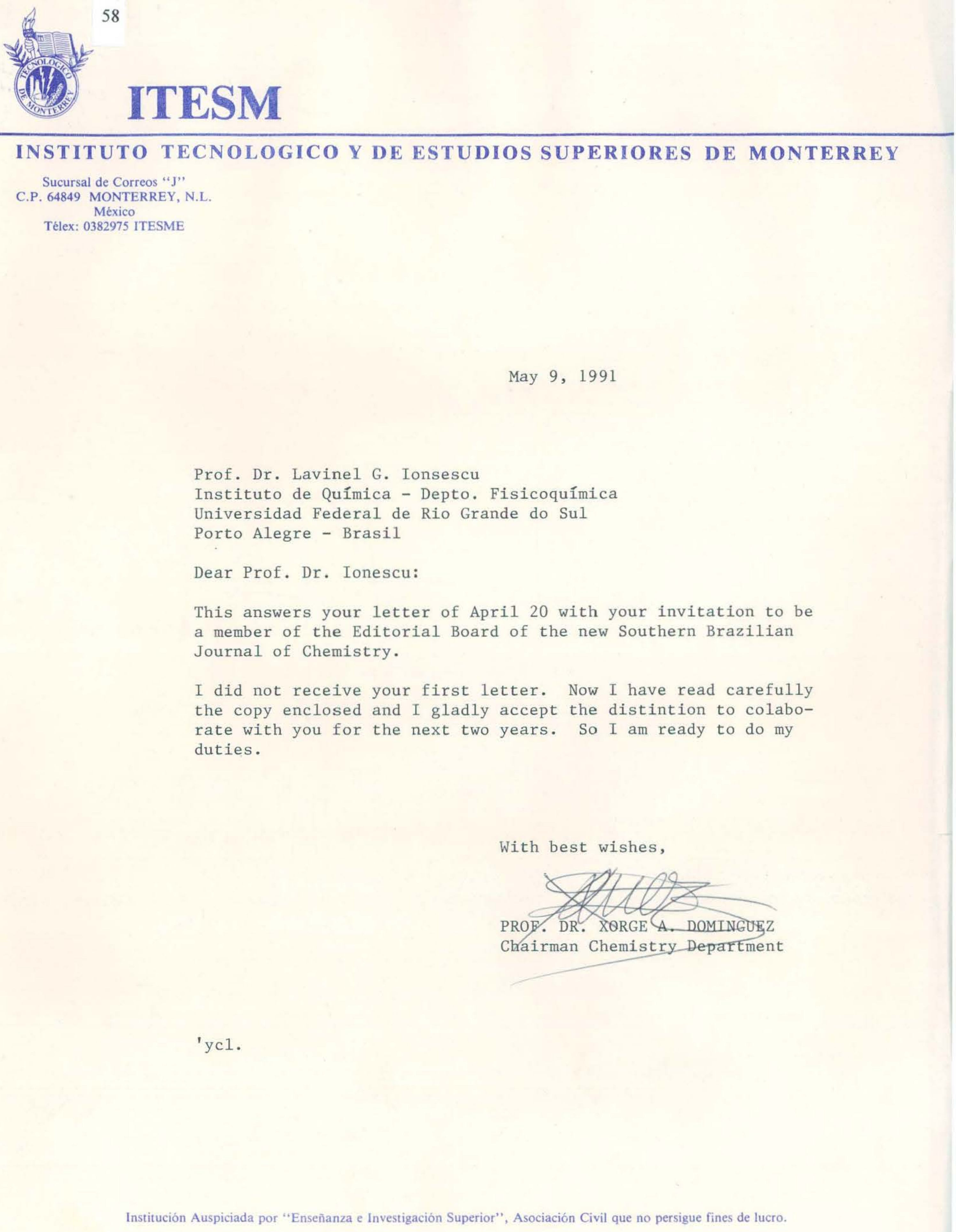
Prof. Dr. Lavinel G. Ionescu
Instituto de Química - Depto. Fisicoquímica
Universidad Federal do Rio Grande do Sul
Porto Alegre, BRASIL

POR AVION

AIR MAIL



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C.P. 64849 MONTERREY, N.L.
México
Télex: 0382975 ITESME

May 9, 1991

Prof. Dr. Lavinel G. Ionsescu
Instituto de Química - Depto. Fisicoquímica
Universidad Federal de Rio Grande do Sul
Porto Alegre - Brasil

Dear Prof. Dr. Ionescu:

This answers your letter of April 20 with your invitation to be a member of the Editorial Board of the new Southern Brazilian Journal of Chemistry.

I did not receive your first letter. Now I have read carefully the copy enclosed and I gladly accept the distintion to colaborate with you for the next two years. So I am ready to do my duties.

With best wishes,

PROF. DR. XORGE A. DOMINGUEZ
Chairman Chemistry Department

'ycl.

Institución Auspiciada por "Enseñanza e Investigación Superior", Asociación Civil que no persigue fines de lucro.

Professor X.A. Dominguez was widely respected in the scientific community. He was a member of the Mexican Chemical Society, American Chemical Society, Swiss Chemical Society, Phytochemical Society of America, National Academy of Scientific Research of Mexico and a fellow of the Royal Chemical Society. He was President of the Northeast Section of the Sociedad de Quimica de México from 1976 to 1978 and gave many invited lectures throughout Europe and the Americas.

He received many awards for excellence in teaching or research in chemistry. Among them we cite the *Romulo Garza Prize for Research* in 1974 and *for Teaching* in 1975, *National Scientific Prize Luis Elizondo* in 1976, *National Education Award* in 1982, *Andrés Manuel Del Rio Award in Chemistry* in 1985, *National Chemical and Pharmaceutical Sciences Award* in 1986 and the *Lázaro Cárdenas Medal* in 1991.

He was regional Editor (1970-1972) and Editor in Chief of the *Revista Latinoaricana de Química* from 1972 to 1991 and member of the Editorial Board of other journals and periodicals including *Revista de la Sociedad Química de México* and *Revista Iberoamericana de Educación Química*.

Prof. Xorge A. Dominguez was Member of the Editorial Board of the *Southern Brazilian Journal of Chemistry* and he gave us valuable advice during the initial stages of this Journal. He was always ready to help, collaborate and fulfill his responsibilities.

MARIO JOSÉ MOLINA, 1995 NOBEL PRIZE IN CHEMISTRY

Mario José Molina was born in Mexico City on March 19, 1943. His father, Roberto Molina Pasquel was a lawyer, a faculty member of the Universidad Nacional Autonoma de México-UNAM and also served as Ambassador of Mexico to Ethiopia, Australia and the Philippines.

He attended elementary school in Mexico City and at the age of eleven went to a boarding school in Switzerland. At the time, according to what Professor M.J. Molina states in his autobiography, he had already decided to become a research chemist. [44]

In 1960 he enrolled in the Chemical Engineering Program of the National University of Mexico-UNAM and in 1965 he obtained the Bachelor Degree in Chemical Engineering.

MARIO JOSÉ MOLINA, 1995 NOBEL LAUREATE IN CHEMISTRY

Mario José Molina spent almost two years (1965-1966) doing graduate studies at the University of Freiburg, Germany, doing research in the kinetics of polymerizations. During his stay in Europe, he also spent some time in Paris studying mathematics and became thoroughly convinced to obtain a good background in mathematics, physics and physical chemistry.

In 1968 he went to the University of California at Berkeley-UCB in order to pursue graduate studies in physical chemistry. His research advisor was Prof. George C. Pimentel, a well known scientist, who studied molecular dynamics with chemical lasers and also was a pioneer in matrix isolation techniques used in the elucidation of molecular structure and bonding of transient species. In 1972, Mario José Molina completed his Ph.D. Degree in Physical Chemistry. His research work involved the investigation of the distribution of internal energy in the products of chemical and photochemical reactions. He summarizes his experience at the University of California at Berkeley as follows:

"My years at Berkeley have been some of the best of my life. I arrived there just after the era of the free-speech movement. I had the opportunity to explore many areas and to engage in exciting scientific research in an intellectually stimulating environment. It was also during this time that I had my first experience dealing with the impact of science and technology on society. I remember that I was dismayed by the fact that high-power chemical lasers were being developed elsewhere as weapons; I wanted to be involved with research that was useful to society, but not for potentially harmful purposes." [44]

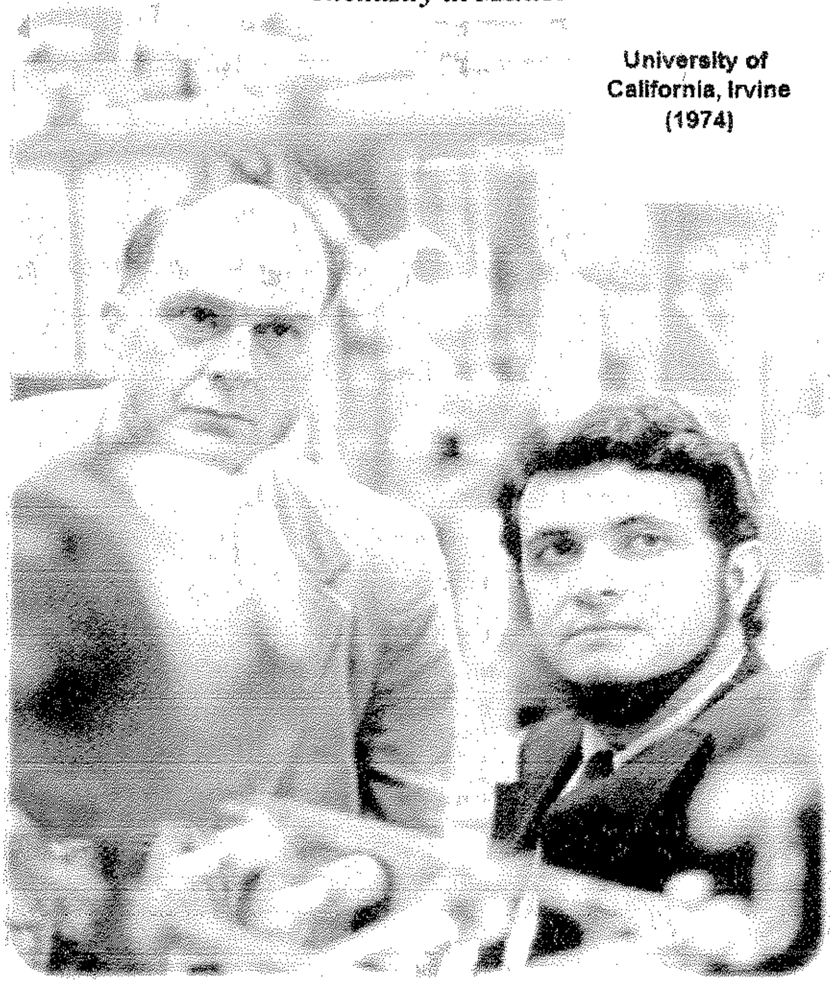
In the fall of 1973, Mario J. Molina joined the group of Professor F. Sherwood Rowland at the University of California at Irvine-UCI, as a Postdoctoral Fellow. It was there that he together with F. Sherwood Rowland developed the Chlorofluorocarbons (CFCs) - Ozone Depletion Theory that later was recognized as a major contribution to science and led to the award of the Nobel Prize in Chemistry in 1995 together with Paul J. Crutzen.

Prof. Dr. Mario José Molina had faculty positions at the Universidad Nacional Autónoma de México-UNAM (1967-68), University of California at Irvine (1975-1982), Massachusetts Institute of Tecnhology (1989-2005), University of California at San Diego and the Center for Atmospheric Sciences of the Scripps Institute of Oceanography (2005-Present).

From 1982 to 1989, Prof. Dr. Mario J. Molina held a non-academic position at the Jet Propulsion Laboratory-JPL in Pasadena, California. His research group at JPL studied the chemistry of stratospheric clouds over Antarctica.

At the present, beside the faculty position at the University of California, San Diego, Prof. Molina also directs a research center in Mexico City that deals with strategic studies in energy and the environment.

The Chlorofluorocarbons (CFCs) – Ozone Depletion Theory involved at first a systematic search for the processes that might destroy the CFCs in the lower atmosphere. However, nothing appeared to affect them. At sufficiently high altitudes, the CFCs were destroyed by solar radiation. Chlorine atoms produced by the decomposition of the CFCs can catalytically destroy ozone.



F. SHERWOOD ROWLAND AND MARIO J. MOLINA IN IRVINE, CALIFORNIA IN 1974.

The role of nitrogen of natural origin in the control of ozone levels in the stratosphere was elucidated by Paul J. Crutzen. What preoccupied Molina and Rowland was the large quantity of CFCs released in the atmosphere by industrial processes, when compared to naturally existing amounts of nitrogen oxides. Mario J. Molina and F. Sherwood Rowland became alarmed at the possibility that continues emission of CFCs into the atmosphere would cause depletion of the Earth's stratospheric ozone layers. Their findings were published in an article that appeared in *Science* on June 28, 1974.[45] The ozone depletion was confirmed by Joseph C. Farman of the Halley Bay Station of the British Antarctic Survey in 1984. The ozone depletion (ozone hole) over Antarctica was documented by Nimbus satellite data in 1986 and many satellite images in the years that followed.

In 1987, the Montreal Protocol, signed by 56 countries agreed to 50% cuts in CFCs use and production. M.J. Molina's feelings about his contribution are summarized as follows in his Nobel Autobiography.[44]

"When I first chose the project to investigate the fate of chlorofluorocarbons in the atmosphere, it was simply out of scientific curiosity. I did not consider at that time the environmental consequences of what Sherry and I had set out to study. I

am heartened and humbled that I was able to do something that not only contributed to our understanding of atmospheric chemistry, but also had a profound impact on the global environment.

One of the very rewarding aspects of my work has been the interaction with a superb group of colleagues and friends in the atmospheric sciences community. I truly value these friendships, many of which go back 20 years or more, and which I expect to continue for many more years to come. I feel that this Nobel Prize represents recognition for the excellent work that has been done by my colleagues and friends in the atmospheric chemistry community on the stratospheric ozone depletion issue."

Besides the 1995 Nobel Prize in Chemistry awarded to him jointly with F. Sherwood Rowland and Paul J. Crutzen, Prof. Dr. Mario J. Molina received many prizes and awards. He is a member of the Pontificial Academy of Science, U.S. National Academy of Sciences, National College of Mexico and received honorary degrees from about twenty universities from different countries.

His current work is related to air quality and global climate changes. Of particular interest is the improvement of air quality in rapidly growing cities, like Mexico City and the investigation of the chemical properties of atmospheric particles and their effect on clouds and climate.

ACKNOWLEDGEMENT

One of us (LGI) gratefully acknowledges financial support received from Pró-Reitoria de Pesquisa e Pós-Graduação – PROPESP of ULBRA (Lutheran University of Brazil) and Sarmisegetusa Research Group, Santa Fe, New Mexico, USA.

REFERENCES

1. M. Roche, *Science, 194*, 806 (1976).
2. G. Weinberg, *Interciencia, 3(2)*, 72 (1978).
3. L. G. Ionescu, Editor *"Anais do 2° Simpósio de História e Filosofia da Ciência – Proceedings of the Second Symposium on Philosophy and History of Science"*, Sociedade Brasileira de Química – Regional do Rio Grande do Sul, Editora Químico Pampeano, Viamão, RS, Brasil, 1990, 76 pp.
4. L. G. Ionescu and J.A. Schufle, "José Luis Casaseca – Founder of the Cuban Institute of Research", *J. Chem. Educ., 55*, 583 (1978).

5. L. G. Ionescu and J. A.Schufle, "Alvaro Raynoso – Father of the Cuban Sugar Technology" *N. Mex. J. Science, 21(1),* 41 (1981).
6. L. G. Ionescu, R.A. Yunes and J.A., Schufle, "Horacio Damianovich, Argentine Pionner in Nobel Gas Chemistry ",., *J. Chem. Educ 59,* 304 (1982).
7. L. G. Ionescu, R.A. Yunes and J.A. Schufle, "Latin American Contribuitions to Chemistry. VI Gustavo Fester, Argentina's Formost Natural Products Chemistry" *N. Mex. Highlands Univ. J., 4(1),* 32 (1983).
8. L. G. Ionescu, "Xorge Alejandro Dominguez, Mexico's Formost Organic Chemistry", *South. Braz. J. Chem., 2,* 1 (1994).
9. L. G. Ionescu and C. A. Perazzolo, "Luis Frederico Leloir – South America's Only Nobel Laureate in Chemistry", *South. Braz. J. Chem., 3,* 1 (1995).
10. L.G. Ionescu, *South. Braz. J. Chem., 4,* 1 (1996).
11. R. Osorio O. "Historia de la Quimica en Colombia", Publ. Geol. Esp., Ingeminas, Bogotá, Colombia, 1982.
12. M.Bargalló, "La Amalgamación de los Minerales de Plata em Hispanoamérica Colonial"Compañia Fundidora de Fierro y Acero de Monterrey, Mexico, 1969.
13. M. Bargalló, "La Mineria y Metalurgia em la América Española durante la Epoca Colonial", Fondo de Cultura Económica, Mexico, D.F., 1955.
14. M.E. Weeks," Discovery of the Elements", Published by the Journal of Chemical Education, Easton, Pa., USA, 1945.
15. L. G. Ionescu, "Romanians in the History of Mexico", in *America Almanach,* Union and League of Romanian American Societies, Inc., P. Lucaci, Ed., Cleveland, Ohio, USA, pp 156-162.
16. J. A. Chamizo, *Rev. Soc. Quim. Mex., 48,* 165-171 (2004).
17. J. A. Chamizo, A. Garritz and M. Kleiche Dray, in "Proceedings 6TH International Conference on the History of Chemistry", European Association for Chemical and Molecular Sciences, Leuven, Belgium, August 28 – September 1, 2007.
18. A. F. Chalmers, "What is This Thing Called Science", Open University Press, Milton Keynes, 1985.
19. J. Bond, "Pre-Columbian Chemistry: A Descriptive Chemistry and Technology From Natural Resources", Tufts University Press, Medford, Ma., USA, 1993.
20. F. A. Encina, "Historia de Chile", Editorial Ercilla, Santiago, Chile, 1985.
21. J. A. Del Busto, "Historia General del Perú Antiguo" Ed. Studium, Lima, Perú, 1970.
22. A. Garritz, Ed., "Química en México. Ayer, Hoy y Mañana", Facultad de Química, Universidad Nacional Autonóma de México – UNAM, México, DF, 1991.
23. B. Ortiz de Montellano, "Aztec Medicine, Health and Nutrition" Rutgers University Press, Picataway, NJ, USA, 1990.
24. T. de la Selva, "De la Química a la Alquimia" La Ciencia desde México, No 118, Secretaria de Educación Publica – SEP, Fondo de la Cultura Económica,

Consejo Nacional de Ciencia y Tecnologia, Mexico, DF, 1993.

25. A. Romo de Vivar, "Química, Universo, Tierra y Vida" La Ciencia desde México, No 51, Secretaria de Educación Publica – SEP, Fondo de la Cultura Económica, Consejo Nacional de Ciencia y Tecnologia, Mexico, DF, 1988.
26. J. A. Chamizo, *Química Mexicana*, Conaculta, Tercer Milenio, México, DF, 2003.
27. L. G. Ionescu and P. C. P. das Neves, Chemical Alloys and Minerals Ocurring Naturally in Meteorites, *South. Braz. J. Chem*, 9(10), 47-62 (2001).
28. R. P. Foster, Editor, "History of Gold Production", Biological Society of Zimbabwe, Rhodesia, Balkema, Rotterdam, Netherland, 1984.
29. B. Ortiz de Montellano, "Empirical Aztec Medicine,", *Science, 188*, 215-220 (1975).
30. http:/www.mexicolore.co.uk
31. V. Navarro and M.L. Villareal, *J. Ethnopharmacology, 53(3)*, 143-147 (1996).
32. L.G. Ionescu, "Antonio de Ulloa, Discoverer of Platinum", *South. Braz. J. Chem., 6(7)*. 1-6 (1998).
33. J. Jorge and J.A. De Ulloa, "*Relación Histórica del Viaje a la América meridional hecho de Orden de S. Mag. para Medir Alguns Grados del Meridiano Terrestre Y Venir por Ellos em Conocioimento de la Verdadera Figura Y Magnitud de la Tierra , com Otras Observaciones Astronómicas y Físicas*", Antonio Marin, Madrid, 1748.
34. J. Jorge and J.A. De Ulloa, "*A Voyage to South America*", Vols. 1,2, Lockyer Davis, London, 1772.
35. C.M. La Condamine, "*Relation abregeé d'un voyage fait dans l'interieur de l'Amérique Meridionale* ", Paris1745.
36. A. Phelps, "*Louisiana, a Record of Expansion*", Houghton, Mifflin and Company, Boston, MA, USA, 1993.
37. A. von Humboldt . "*Essai Politique sur le Royame de la Nouvelle Espagne*", Schoell, Paris, 1811.
38. L. G. Ionescu, "Andrés Manuel del Rio, Discoverer of Vanadium", *South. Braz. J. Chem., 5(5),* 1-6 (1997).
39. A. M. Del Rio, "*Tablas Mineralogicas de Karsten*", Mexico, 1804.
40. A. Cabanilles, *Anal.Cienc. Nat. Madrid,6*, 16 (1803).
41. A .von Humboldt, *Gilb. Ann., 18*, 118 (1804).
42. H. V. Collet-Descotils, *Ann. Chim. Phys., 1(53)*, 268 (1805).
43. O. Wallach, "Briefenwechsel zwischen J. Berzelius und F. Wöhler", Vols. 1,2, Verlag Wilhelm Engelmann, Leipzig, 1901.
44. M. Molina, Autobiography, The Nobel Foundation, 2006.
45. M. Molina and F. Sherwood Rowland, "Stratospheric Sink for Chlorofluoromethanes: Chlorine Atoms Catalyzed Destruction of Ozone", *Nature, 249*, 810-813 (197).

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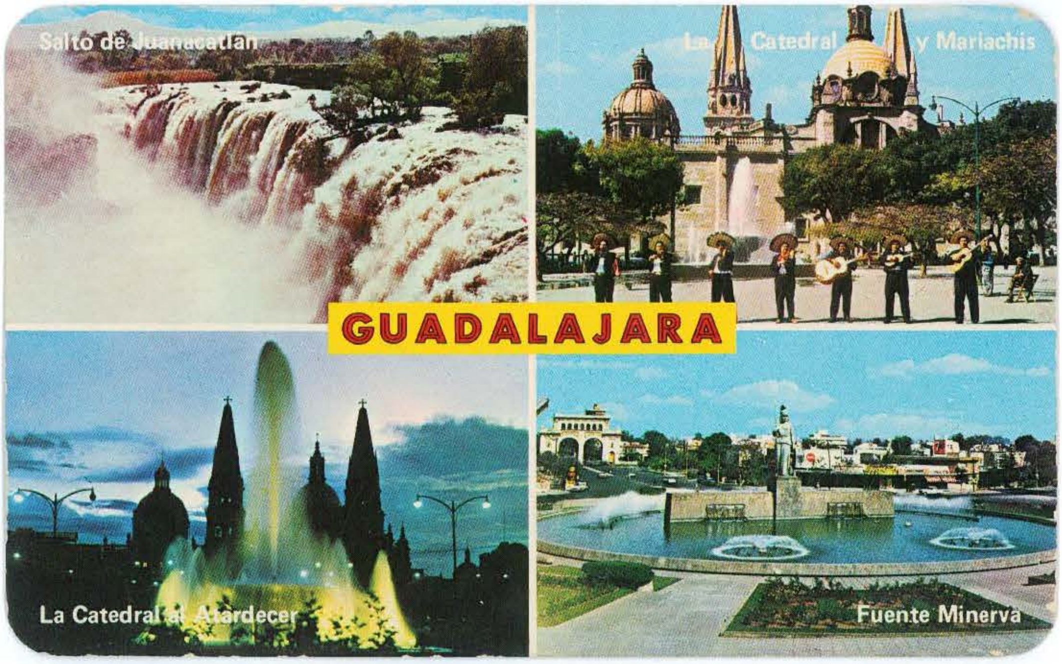
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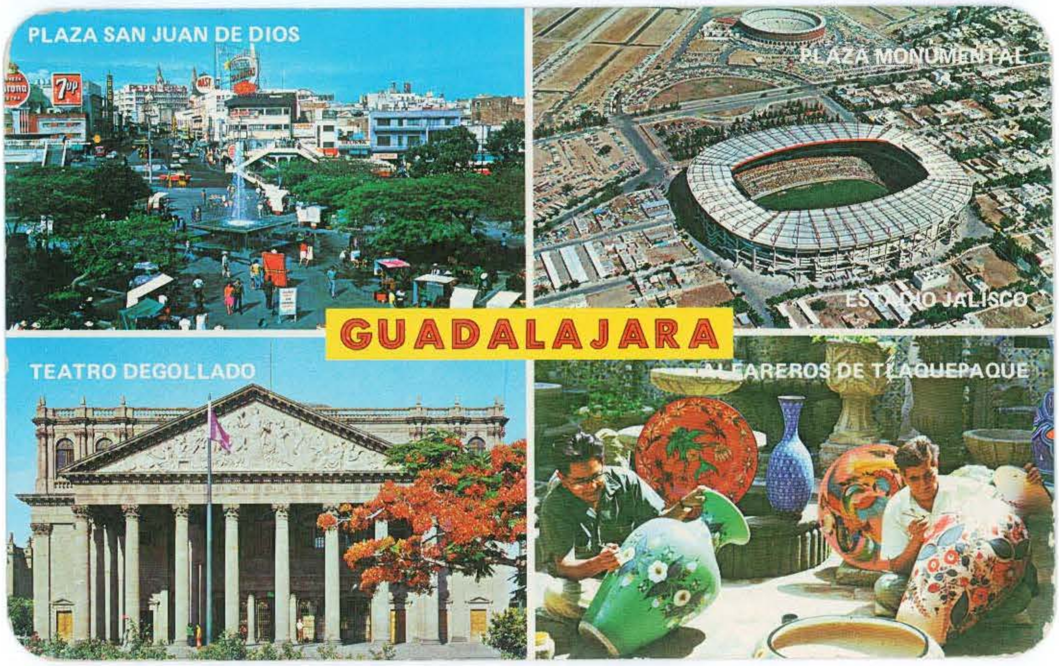
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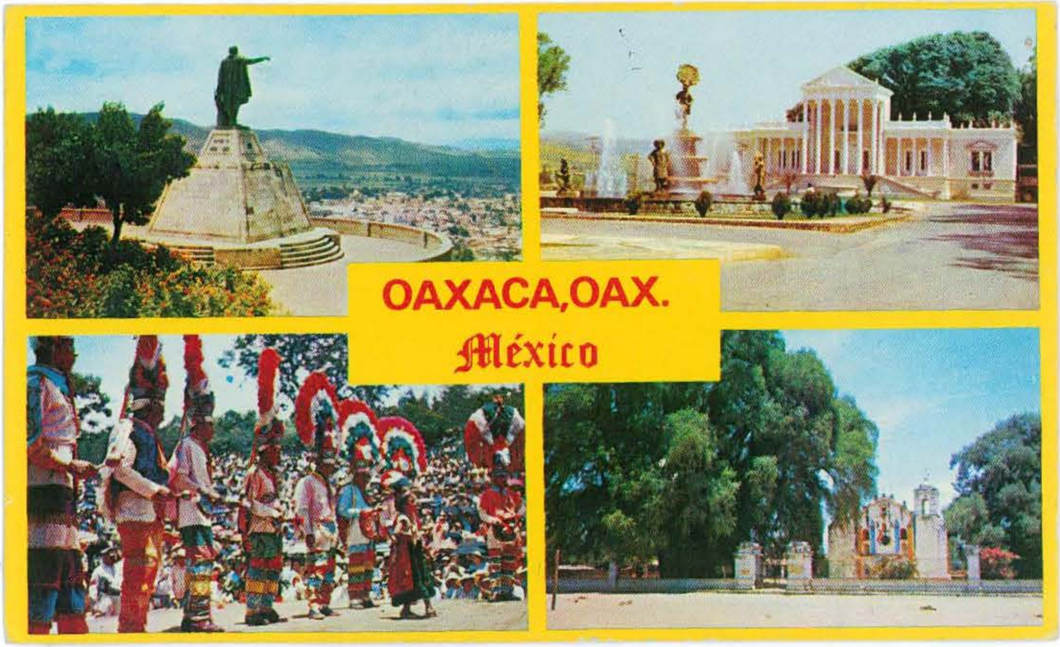
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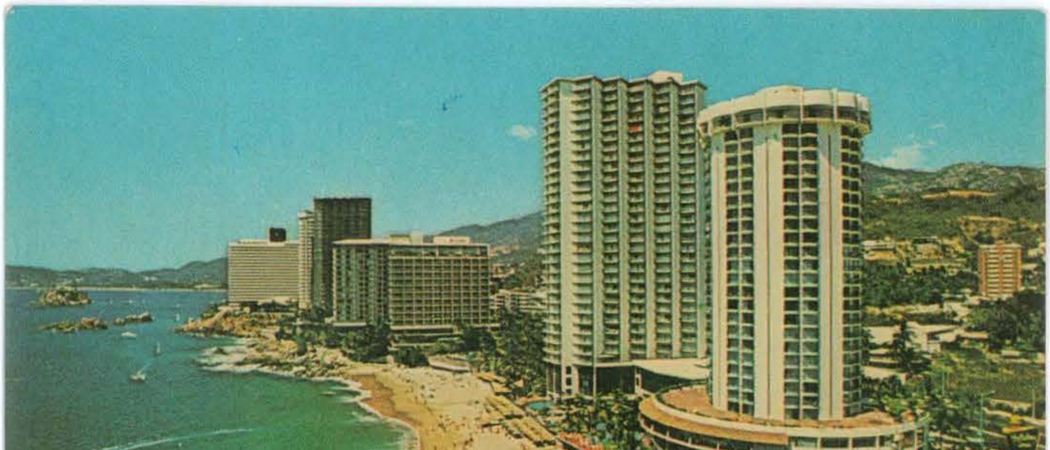
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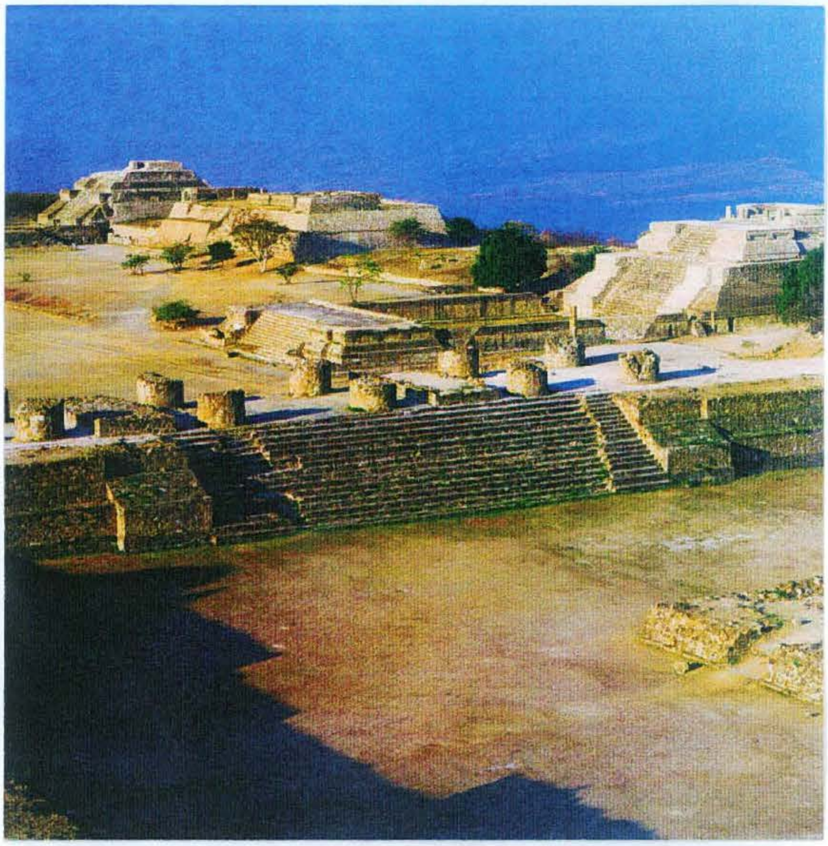

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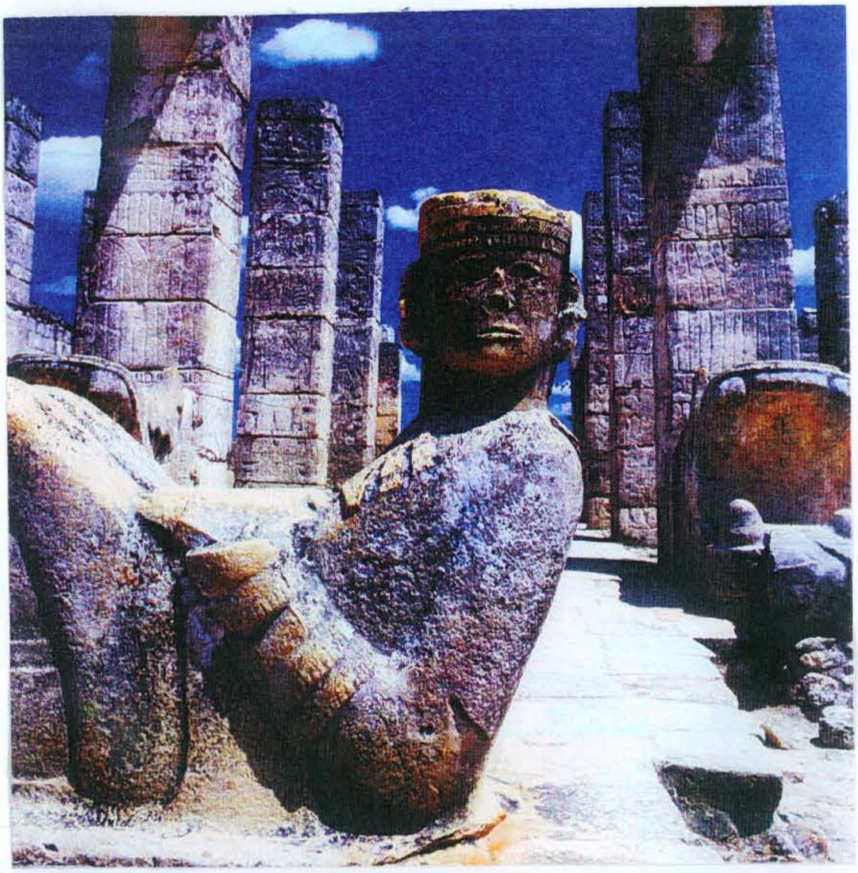

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