INDUSTRIAL HYGIENE SURVEY

Texas Smelting & Refining
Division of National Lead Industries
Laredo, Texas

SURVEY DATE

March 1-5, 1976

SURVEY CONDUCTED BY

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Place Visited:	Texas Smelting & Refining Division of National Lead Industries P.O. Box 559 Laredo, Texas 78040 Telephone: (512) 722-2486
Company People Contacted:	C.H. Hornedo, Plant Manager Albert L. Belcher, Corporate Industrial Hygienist, NLI, Inc. Hightstown, N.J. (609) 448-3200
Union:	United Steel Workers
Purpose of Visit:	To conduct an industrial hygiene survey and to collect personal samples for the determination of arsenic and antimony.

INTRODUCTION AND GENERAL COMMENTS

The Texas Smelting and Refining Division of National Lead Industries is located on the northern perimeter of Laredo, Texas on a 45 acre tract of land. About five or six structures make up the plant facilities. In addition, on the plant site are three or four residences where the plant manager and others of the supervisory staff live.

The plant operates around the clock seven days a week. The employees are represented by the United Steel Workers Union.

The N.L. Industries has corporate industrial hygiene, medical and safety personnel who cover activities in this plant. There is a safety committee at this site, administered by one of the supervisors. Air samples are collected at irregular intervals by the corporate industrial hygienist. A general area sampling survey on this plant was conducted by NIOSH in 1975, at which time the oxide production facilities were not operating. The purpose of the current survey was to take personal samples on essentially the entire work population to determine exposure to antimony (Sb) and to arsenic (As) which occurs as an impurity in the antimony oxide ore, at a time when the plant was in full operation.

DESCRIPTION OF PLANT PROCESS AND PRODUCT LINE

This plant, with a population of about 120 employees, recovers antimony metal and oxide from ore imported from a company-owned mine in Mexico, as well as from ore purchased from Honduras, and other Central and South American countries. It is apparently the only producer of antimony metal

in the United States. The manufacturing process described fully in the previous 1975 report is described also in a flow sheet, appended. The ore is mixed with coke, flux, and iron ore and reacted in a blast furnace (singles furnace) to produce a metal of approximately 85-90% antimony content.

Next the metal goes into another furnace (doubling furnace), where it is further refined to approximately 95-98%. From here it goes to the starring furnace to produce 99.5% antimony metal which is cast into pigs. From this point the metal may be sold as is or it may go either to the Lone Star Furnace to produce 99.8% metal or to the oxide furnace. In the oxide furnace, the antimony metal is melted, and then air is blown through the molten metal forming antimony oxide which is volatilized and condensed as a fine powder, Sb_2O_3. This powder is collected in bag collectors, then bagged for shipment to customers.

Appended is a flow chart of Antimony Metal and Oxide Processing described above. All furnaces and processes are equipped with local exhaust ventilation which is described in detail in the previous 1975 report.

GENERAL IMPRESSIONS AND OBSERVATIONS

In the previous survey in 1975 the plant was found to be carrying out a relatively clean operation, in spite of the fact that some of the furnaces and equipment have been in operation since 1930. During the present survey it was obvious that the plant had deteriorated. According to the company this is due to depressed business conditions during the past year which necessitated a reduction in force. When business improved and

employees where recalled, many of the skilled maintenance and supervisory employees did not return. Because of absence of these skilled personnel, the plant had not at the time of this survey attained its former good operating practice.

As in the previous survey each employee carried a half mask respirator with approved cartridges which he wore practically 100% of the time he was in the production area. Respirator training of new employees, appears to be needed since many of the employees were observed wearing their respirators with only one strap fastened.

Besides respirators, the employees are supplied with and wear hard hats, safety glasses and shoes. Coveralls are supplied to those working in the baghouses.

As a result of a recommendation made following the 1975 survey, laundry facilities have been installed on the plant site and now all work clothes are laundered "in-house". There is no necessity to take work clothes to the home for laundering.

Samples from the two employees who worked in the singles furnace baghouse were greater than 10 mg/m^3 Sb - They wore full face piece canister type masks, so actual exposure was probably minimal.

Around this same baghouse area, there was a sulfur like aroma which was neither SO_2 nor H_2S. This was believed to be carbonyl sulfide; however, no analytical means were available to verify this postulation.

SURVEY PROCEDURES AND RESULTS

During this survey Breathing Zone (BZ) samples were collected on 55 employees over their 8 hour shift using personal sampling pumps operating at 2.0 lpm, equipped with Millipore 37 mm, 0.8 µm pore size, AA filters. The collected samples were analyzed for Sb and As.

RESULTS

The samples results for arsenic and antimony by job and location for both the 1975 and 1976 survey are appended in Tables I-III. Result ranges tabulated below from the 1976 survey are compared with result ranges from the General Area Samples (GA) taken during the 1975 NIOSH survey in the same facility at which time the oxide production unit was not in operation.

RANGE OF SAMPLE RESULTS FROM TWO INDUSTRIAL HYGIENE SURVEYS**

Survey	Sb, mg/m^3	As, mg/m^3
1975 GA Survey	0.14 - 2.02	0.0006 - 0.004
1976 BZ Survey	0.05 - 6.21	0.001 - 0.037*

DISCUSSION OF RESULTS

Even though the above tabulation represents both GA and BZ sample results which are not necessarily strictly comparable, the higher values found in the BZ samples during this survey are indicative of greater exposure to personnel, resulting from the deteriorated industrial hygiene maintenance and operating conditions in the plant. During the present survey all plant operations including the oxide production facility

* An As value of 0.160 mg/m^3 believed to be in error was dropped.
** Based on eight hour samples.

were in operation. The oxide bagging equipment, recently replaced, was creating some dusting. In addition there was significance air pollution contribution of the doubles furnace which was the major source of air pollution in the plant area.

Besides visible fumes being present, significant concentrations of SO_2 were found near the doubles furnace. Drager tubes indicated from 2-20 ppm SO_2, with an average of the eight tubes collected showing 5.3 ppm (see Table IV). During the 1975 survey there were essentially no detectable SO_2 levels.

A statistical analysis of the monitoring data broken down into six job categories is described in summary Table III, appended. The mean exposure values to Sb and As for the oxide operation, 2.23 mg/m^3 (Sb) and 0.0022 mg/m^3 (As) respectively, were the largest exposures in the plant. These were more than four times the OSHA standard for Sb (0.5 mg/m^3) and more than five times the OSHA recommended standard [1] for As (0.004 mg/m^3), but below the present OSHA standard [2] for As (0.5 mg/m^3). The mean values of exposures to Sb in all other operations, even though lower than these found in the oxide operation, were also above the standard referred to above. With As, however, the mean values in all other operations were below the current OSHA standard of 0.5 mg/m^3, but all above the recommended OSHA standard of 0.004 mg/m^3.

The standard deviation and range of individual sample values for the six job categories are large, indicating that exposure of a worker to Sb and As in these operations has considerable variation.

SUMMARY AND CONCLUSIONS

From the sample data collected in this survey, the mean concentration of the antimony and arsenic exposures for all employee classifications were found to exceed the current OSHA standard of 0.5 mg Sb/m^3 and the recommended OSHA standard of .004 mg As/m^3. However, the means of all arsenic exposures were found to be below the current OSHA standard of .5 mg/m^3. The highest exposures to antimony and arsenic were among the antimony oxide operators.

Intermittent exposures to sulfur dioxide measured with a Drager tube reached peak values of 25 ppm, with an average of eight samples showing over 5 ppm. It is not believed that under more normal operation conditions with properly maintained furnaces that the SO_2 exposure will run this high.

In general, maintenance and operating procedures were not up to the standards attained at the time of the previous survey. As discussed herein the present deteriorated operating condition was brought about by the recent turnover of personnel which resulted in many new and untrained employees on the plant site. Evidence of this is revealed in the higher exposure values found in this survey over those resulting from the 1975 survey.

Since arsenic exposures did not exceed the recommended OSHA standard in the 1975 survey and since the plant at that time was probably more representaive of its condition during past years, antimony has been the principal exposure. In view of these facts, this plant could be an acceptable candidate for an epidemiological study of exposure to antimony.

RECOMMENDATIONS

1. In the laboratory the odor of H_2S was definitely strong and irritating. The laboratory hoods should probably operate continuously so that any H_2S used will be exhausted promptly.

2. In the blacksmith shop considerable smoke was generated. There could be a CO problem here but no test was made for CO. The hood was in need of repair and possible redesign so as to increase the ventilation.

3. Considerable problems were observed in connection with the doubles furnace which fumes almost continuously. Immediate attention to ventilation and maintenance on this equipment would contribute greatly to better hygienic conditions.

REFERENCES

1. D.O.L. Occupational Safety and Health Standards, Federal Register p. 3395, January 21, 1975.

2. Ibid, Federal Register, p. 2351, June 27, 1974.

Table I - Personal Air Sample Results
Texas Smelting & Refinery (NLI)
Laredo, Texas
March, 1976

Sample #	Operation	Time On	Time Off	Total Time Min.	Flow Rate lpm	Vol. air m^3	Sb			As			
							Mg/ Sample	Mg/m^3	% TLV	Mg/ Sample	Mg/m^3	% TLV	% Proposed TLV
	Oxide												
051	Fce Operator	350	1115	445	2.0	0.890	0.08	0.090	18	0.007	0.008	1.6	200
207	Fce Operator	325	1109	464		0.928	2.77	2.980	596	0.020	0.022	4.4	550
059	Fce Operator	752	332	460		0.920	2.82	3.070	614	0.034	0.037	7.4	925
319	Fce Operator	746	337	471		0.942	1.89	2.010	402	0.016	0.017	3.4	425
226	Packer	338	1115	457		0.914	2.37	2.590	518	0.146	0.160	320	4000
295	Packer	747	337	470		0.940	2.45	2.610	522	0.023	0.024	4.8	600
	Singles Fee												
153	Tapper	720	345	505	2.0	1.010	1.64	1.62	324	0.005	0.005	1.0	125
239	Tapper	750	350	480		0.960	1.17	1.22	244	0.008	0.008	1.6	200
286	Tapper	335	1121	466		0.932	0.38	0.41	82	0.010	0.010	2.0	225
227	Conveyor Operator	756	336	460		0.920	1.68	1.83	366	0.012	0.013	2.6	325
	Dbles. Fee												
293	Fce Operator	428	1109	401	2.0	0.802	1.04	1.30	260	0.002	0.002	0.4	50
138	Fce Operator	758	334	456		0.912	0.81	0.89	178	0.003	0.003	0.6	75
274	Fce Operator	753	310	437		0.874	1.84	2.10	420	0.009	0.010	2.0	250
171	Fce Helper	805	340	455		0.910	1.38	1.52	304	0.006	0.007	1.4	175
	Maintenance												
343	Blacksmith	830	341	431	2.0	0.862	0.13	0.15	30	0.001	0.001	0.2	25
249	Maint. Man-Shop	807	407	480		0.960	0.11	0.11	22	0.001	0.001	0.2	25
324	Mechanic	813	340	447		0.894	0.08	0.09	18	0.001	0.001	0.2	25
150	Mechanic Shop	813	339	440		0.892	0.08	0.09	18	0.001	0.001	0.2	25
144	Maint. Welder	814	341	447		0.894	0.08	0.09	18	0.002	0.002	0.4	50
186	Bricklayer	815	353	458		0.916	0.64	0.70	140	0.002	0.002	0.4	50
229	Bricklayer	803	353	470		0.940	5.89	6.21	1242	0.016	0.017	3.4	425
238	Bricklayer	343	1205	442		0.884	0.18	0.20	40	0.002	0.002	0.4	50

Table I - Personal Air sample Results
(continued)

Sample #	Operation	Time On	Time Off	Total Time Min.	Flow Rate lpm	Vol. air m^3	Sb			As			
							Mg/ Sample	Mg/m^3	% TLV	Mg/ Sample	Mg/m^3	% TLV	% Proposed TLV
	Laborers												
063	Laborer	345	1105	440	2.0	0.880	0.08	0.09	18	0.001	0.001	0.2	25
030	Laborer	810	338	448		0.896	1.46	1.63	326	0.012	0.013	2.6	325
003	Laborer	812	343	451		0.902	1.73	1.92	384	0.008	0.009	1.8	225
031	Laborer	800	357	477		0.954	0.90	0.94	188	0.002	0.002	0.4	50
158	Laborer	745	350	485		0.970	1.30	1.34	268	0.040	0.041	8.2	1025
181	Laborer	805	407	482		0.964	0.37	0.38	76	0.004	0.004	0.8	100
187	Laborer	800	337	457		0.914	1.47	1.61	322	0.012	0.013	2.6	325
139	Laborer	323	1109	466		0.932	0.62	0.67	134	0.005	0.005	1.0	125
191	Laborer	323	1130	487		0.974	1.04	1.07	214	0.005	0.005	1.0	125
199	Laborer	354	1128	454	2.0	0.908	1.45	1.600	320	0.008	0.009	1.8	225
205	Laborer away from yard most of day	759	335	456		0.912	0.21	0.230	46	0.003	0.003	0.6	75
209	Laborer	748	336	468		0.936	0.92	0.980	196	0.007	0.007	0.2	25
211	Laborer	752	333	461		0.922	0.11	0.120	24	0.001	0.001	0.2	25
232	Laborer	755	302	427		0.854	0.12	0.140	28	0.001	0.001	0.2	25
256	Laborer	811	345	454		0.908	1.71	1.880	376	0.009	0.010	2.0	225
261	Laborer	759	337	458		0.916	1.85	2.100	420	0.027	0.029	5.8	725
262	Laborer	801	334	453		0.906	1.12	1.240	248	0.007	0.008	1.6	200
263	Laborer	809	333	443		0.886	0.42	0.470	94	0.002	0.002	0.4	50
251	Laborer	353	1112	439		0.878	1.44	1.640	328	0.010	0.011	2.2	275
301	Laborer	812	335	441		0.882	4.33	4.910	982	0.022	0.025	5.0	625
322	Laborer	753	332	459		0.918	1.40	1.530	306	0.008	0.009	1.8	225
335	Laborer	342	1112	450		0.900	1.11	1.230	246	0.004	0.004	0.8	100
	Miscellaneous												
136	Sweeper-Yard	803	341	458	2.0	0.916	3.43	3.740	748	0.043	0.047	9.4	1175
180	Fork Lift Operator	754	338	464		0.928	0.54	0.580	116	0.002	0.002	0.4	50
233	Gardner	830	353	443		0.886	0.04	0.050	10	0.001	0.001	0.2	25
202	Scale Operator	758	337	459		0.918	1.20	1.210	262	0.009	0.009	1.8	225
305	Warehouse Operator	806	341	455		0.910	0.42	0.460	92	0.003	0.003	0.6	75
317	Warehouse Operator	808	340	452		0.904	0.45	0.500	100	0.003	0.003	0.6	75

Table I - Personal Air Sample Results
(continued)

Sample #	Operation	Time On	Time Off	Total Time Min.	Flow Rate lpm	Vol. air m^3	Sb			As			
							Mg/ Sample	Mg/m^3	% TLV	Mg/ Sample	Mg/m^3	% TLV	% Proposed TLV
	Men in Bag Houses 2 Hours - Full Face Canister Type Mask Worn												
344	Oxide Fee Operator	815	312	428	2.0	0.856	9.30	10.86		0.076	0.089		
234	Laborer	339	1215	456		0.912	9.34	10.24		0.039	0.044		
	NIOSH Sampler												
201	Gary White			255	2.0	0.510	0.35	0.69	138	0.001	0.002	0.4	50
264	Gary White	820	220	360		0.720	1.38	1.92	385	0.006	0.008	1.6	200
	Current OSHA Standard							0.5		0.5			
	Proposed OSHA Standard									0.004			

TABLE II

General Area Sample Results
Texas Smelting and Refining (NLI)
Laredo, Texas
April 21-22, 1975

Location	Time Off	Time On	Total minutes	Flow rate, lpm	Flow m^3	Sb Mg/m^3	As Mg/m^3
Sample No. 1 (Pump No. 31) Blast Furnace	1637	0903	454	2.0	0.91	0.11	0.0007
Sample No. 2 (Pump No. 175) Slag Tapping-Blast Furn.	1638	0904	454	2.0	0.91	0.26	0.0012
Sample No. 3 (Pump 198) Slag Tapping-Blast Furn.	1640	0905	455	2.0	0.91	1.14	0.0024
Sample No. 4 (Pump 24) Doubling Furnace #2	1643	0912	451	2.0	0.90	1.13	0.0027
Sample No. 5 (Pump 189) Starring Furnace #1	1643	0915	458	2.0	0.92	1.12	0.0034
Sample No. 6 (Pump 133) Starring Furnace #2	1644	0917	457	2.0	0.91	0.52	0.0021
Sample No. 7 (Pump 82) Casting Area	1646	0923	453	2.0	0.91	2.02	0.0040
Sample No. 8 (Pump 89) Warehouse	1648	0927	451	2.0	0.90	0.61	0.0018
Sample No. 9 (Pump 85) Burner end of the #1 Starring Furnace	1649	0932	437	2.0	0.87	1.24	0.0029
Sample No. 10 (Pump 224) Oxide Furnace	1651	0935	436	2.0	0.87	0.14	0.0011
Sample No 11 (Pump 196) Charge Scale	1636	0939	417	2.0	0.83	0.36	0.0014
Sample No. 12 (Pump 18) Change Room	1654	0942	432	2.0	0.86	0.54	0.0006

TABLE III

Statistical Summary of Results of Sampling for Sb and As

By Plant Operations

Texas Smelting and Refining (NLI) - Laredo, Texas - March, 1976

Operation	No. of Samples	Sb			As		
		Range mg/m^3	Mean Mg/m^3	Std. Dev.	Range mg/m^3	Mean mg/m^3	Std.
Oxide Mfg.	6	0.09-3.07	2.23	1.11	0.008-0.037*	0.022	0.011
Doubles Fee	4	0.89-2.10	1.45	0.50	0.002- 0.010	0.006	0.004
Singles Fee	4	0.41-1.83	1.27	0.63	0.005-0.013	0.009	0.003
Maintenance	9	0.09-6.21	0.94	2.00	0.001-0.018	0.005	0.007
Laborers	22	0.09-4.91	1.26	1.08	0.001-0.041	0.009	0.010
Misc.	6	0.05-3.74	1.11	1.35	0.001-0.047	0.010	0.020

*An As value of 0.160 mg/m^3 believed to be in error was dropped from the mean.

ANTIMONY METAL AND OXIDE PROCESSING FLOW SHEET