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# Environmental Assessment of Melting, Inoculation and Pouring

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## ABSTRACT

*Four foundry processes — cupola melting, electric arc furnace (EAF) melting, magnesium inoculation, and pouring — were studied using EPA/IERL-RTP Level 1 Assessment Methodology. This methodology is used to determine the approximate amounts of a wide range of chemical compound classes in the stream sampled. This information can be used to assist in setting priorities for future research efforts.*

*Samples were obtained (before and after emission control devices) for fume generated during inoculation and pouring, from both the cupola and the EAF. The emission control device was a baghouse. The concentrations of chemical classes found were compared to the Discharge Multimedia Environmental Goals (DMEG) established by EPA/IERL-RTP. Significant findings are: 1) the concentration of both halogenated aliphatic and halogenated aromatic organic compound classes exceed the DMEG for all four processes, 2) chromium in excess of the DMEG value was present in pouring, inoculation, and EAF emissions, and 3) arsenic in excess of the DMEG value was present in the cupola emissions. The data indicate the possible presence of small amounts of polynuclear aromatic hydrocarbons (PNA) in the emissions from all four processes.*

## INTRODUCTION

Previous laboratory experiments demonstrated the presence of polynuclear aromatic (PNA) compounds in pouring emissions, but no quantitative estimates were made.[1] This has generated a concern about several sources of foundry emissions. A previous study[2] of the shakeout found organic emissions of 0.6 kg/Mg (1.2 lb/t). Sophisticated analytical methods did not detect significant quantities of polynuclear aromatic compounds of environmental or health concern. Pouring is the next logical casting process to examine the PNAs because it is the next highest emitter of organic compounds.

The purpose of this study was to perform an environmental assessment of pouring, cupola, EAF, and inoculation emissions. In the first three processes the organic emissions were the major concern as they had not been assessed before. Inoculation was of interest because of the possibility of rare earth element emissions, which were found previously[2] in the shakeout emissions.

### Sampling and Analytical Results

Permission to allow sampling was obtained from four foundries, one for each process, which met the criteria of:

1) representatives of the site of the industry in general,
2) quality of operation,
3) quality of construction and maintenance of equipment, and
4) operating at the time of sampling.

Pouring emissions were sampled at a large foundry making gray iron automotive parts in typical greensand molds without cores. The sample was obtained prior to the pollution control device.

The inoculation process was sampled at a large ductile iron casting operation which employed multiple plunging stations with excellent fume control. The sample was obtained prior to the control device.

The cupola sampled was typical of a small foundry, melting 9 to 11 Mg/h (10 to 12 t/h). The sample was obtained from the exhaust stack of a baghouse.

The electric arc furnace was sampled at a steel foundry which was melting plain carbon steel in 4.5-Mg (5-ton) furnaces. Again, the control of emissions was excellent. The sample was obtained from the baghouse exhaust stack.

All samples were acquired with the Source Assessment Sampling System (SASS).[3] This unit draws the gas sample in through a button-hook nozzle and conveys it via a heated tube to a series of three cyclones in an oven. The cyclones separate the particulate into approximately > 10 μm, 10 to 3 μm, and 3 to 1 μm size cuts. The sample is then passed through a fiberglass filter to remove the < 1 μm particulates, cooled, and passed through a cartridge of XAD-2 resin to adsorb organic materials. After the organic vapors are removed, the collected gas passes through a series of reagent bubblers to remove inorganics. Since a constant flow rate through the cyclones is required to achieve good particle size separation, sampling at 100 percent isokinetic is generally not possible.

All procedures were according to the recommended practices found in *IERL-RTP Procedures Manual, Level 1 Environmental Assessment* (Second Edition).[3] The chemical analysis technique used for Level 1 Assessment is designed to:

1) identify the presence of a chemical family category,
2) enable compound identification in some cases where there is no chemical interference,
3) make the error of indicating the presence of a category, even if absent, rather than indicating the absence even if present,
4) estimate the quantities present within a factor of 1/3 to 3 times the actual stream concentration.

The philosophy behind this is that if a "clean bill of health" is indicated, then no concern exists. If a problem is indicated, then more specialized examination is merited. While this approach does not satisfy all interests, it is the only economically feasible method of identifying anything that might be present, no matter what, in a sample of unknown nature. Better methods are possible if it is assumed that the nature of the sample is known, but Level 1 Assessments have revealed unexpected results in many cases. For example, in this study the method revealed organic emissions from magnesium inoculation, something few chemists or metallurgists would expect.

The possibility exists that unexpected results, such as may be found by Level 1 techniques, could be used for product improvement.

*Table 1. Summary of Particulate Data*

| Sample Site | Uncontrolled | | | Controlled | | |
|---|---|---|---|---|---|---|
| | P | I | SO | SO | C | E |
| Air flow rate, $m^3$/min | 1,337 | 262 | 635 | 867 | 630 | 860 |
| Particulate concentration, mg/$m^3$ | 15.2 | 99.7 | 1,996 | 8.9 | ND[b] | ND |
| Particulate emission factor, g/Mg processed | 66.6 | 55.7 | 7,010 | 43.4 | | |

[a]Sampled at 204°C (400°F). Thus, some organic matter may have distilled off of the particulate.

[b]None detected.

*Table 2. Summary of Organic Emissions*

| Sample site | Uncontrolled | | | Controlled | | |
|---|---|---|---|---|---|---|
| | P | I | SO | SO | C | E |
| Air flow, $m^3$/min | 1,337 | 262 | 635 | 857 | 630 | 860 |
| Total organic concentration, mg/$m^3$ | 15.5 | 4.3 | 174.6 | 105.2 | 26.6 | 9.2 |
| Total organic generated, g/Mg processed | 68.1 | 2.6 | 614 | 512 | 90.4 | 173.7 |

## RESULTS

To obtain a better perspective of the pollution potential of the processes studied it is useful to have side-by-side presentation of the overall testing results. Table 1 presents the uncontrolled particulate emissions from pouring (P), inoculation (I), shakeout (SO), and the controlled (scrubbed) shakeout emission, cupola (C), and electric arc furnace (E). The shakeout results are taken from a previous study of iron foundries.[2]

Table 1 shows that in terms of particulate generated per megagram (Mg) processed, the shakeout exceeds the pouring and inoculation by two orders of magnitude. The fumes generated during pouring and inoculation are roughly equal to the wet scrubbed emissions from the shakeout. No detectable particulate matter was found in the baghouse emissions from the cupola and EAF.

Table 2 presents the total organic emissions found from the same sources. It shows that the organic generated, on a g/Mg basis, during shakeout is also greater than that generated during pouring and inoculation by factors of about 10 and 200, respectively. The shakeout also had higher levels of controlled organic emissions, g/Mg basis, than the cupola or EAF. The uncontrolled pouring emissions were of the same magnitude as the controlled cupola emissions.

For the four processes tested in this study, i. e., excluding shakeout, the cupola produced the highest concentration of organic matter. It should be noted, however, that the concentration of organic compounds will depend on the system air flow.

On a production basis, the electric arc furnace emitted the most organic per ton of metal processed. The quality of scrap used will have some effect. If the electric arc furnace (EAF) is clean and is loaded with completely clean scrap, then no emission of organic compounds would be expected, except for those synthesized in the electric arc. Thus, the major portion of organic emissions from the EAF may be attributed to dirty scrap.

Inoculation is a completely inorganic process and thus would be expected not to produce any organic compounds. As Table 2 shows, a low level of organic matter was measured. While the production of methane and simple organics is possible under reducing conditions, from the carbon in the iron, the synthesis of larger organic compounds that would be adsorbed onto XAD-2 resin is not easily conceivable under the oxidizing conditions of magnesium inoculation.

Table 3 compares the amount of organic extracted from the particulate of the processes previously described with each other and with the organic matter captured in the XAD-2 resin. This implies that most of the organic matter is low boiling point material. Particulate matter was collected at 204C (400F).

Table 4 is a summary and comparison of sampling data for the four processes examined in this study.

*Table 3. Organic Extractables*

| Type of Sample | Process Sampled | | | | |
|---|---|---|---|---|---|
| | | Uncontrolled | | Controlled | |
| | SO | P | I | C | E |
| | | Concentrations, mg/m$^3$ | | | |
| Filter (< 1 μm)[a] | 0 | composite particulate | composite particulate | NA[b] | NA |
| 1-3 μm[a] | 0 | | | NA | NA |
| 3-10 μm[a] | 0.12 | | | NA | NA |
| > 10 μm[a] | 0.82 | | | NA | NA |
| Probe[a] | | 1.22 | 0.229 | NA | NA |
| XAD-2 | 173.67 | 14.29 | 4.355 | 26.54 | 9.19 |
| Total | 174.61 | 15.51 | 4.65 | 26.54 | 9.19 |
| | | Concentrations, g/Mg processed | | | |
| Filter (< 1 μm)[a] | 0 | | | NA | NA |
| 1-3 μm[a] | 0 | | | NA | NA |
| 3-10 μm[a] | 0.42 | | | NA | NA |
| > 10 μm[a] | 2.88 | | | NA | NA |
| Probe[a] | | 5.36 | 0.1671 | NA | NA |
| XAD-2 | 614 | 62.76 | 2.433 | 90.422 | 173.7 |
| Total | 614 | 68.12 | 2.600 | 90.422 | 173.7 |

[a]Organic remaining on particulate. Particulate collected at 204°C (400°F).
[b]Not analyzed--insufficient sample collected.

*Table 4. Summary of Sampling Data*

| Sample | P | I | C | E |
|---|---|---|---|---|
| Date of test | 3/11/81 | 2/11/81 | 3/25/81 | 2/25/81 |
| Volume of gas sampled, m$^3$ | 27.84 | 26.41 | 24.66 | 29.27 |
| Duct gas temperature, °C | 33 | 40 | 178 | 31 |
| Duct gas pressure, cm Hg | 74.60 | 73.81 | 75.74 | 73.58 |
| Duct gas molecular wt., dry | 28.84 | 28.84 | 29.60 | 28.84 |
| Duct gas moisture, % | 3 | 3 | 15 | 3 |
| Duct gas velocity, m/sec | 20.94 | 16.95 | 16.34 | 17.98 |
| Duct gas flow rate, m$^3$/sec | 22.29 | 4.360 | 10.50 | 14.34 |
| Total sampling time, min | 250 | 245 | 250 | 240 |
| SASS train flow rate, m$^3$/sec | 0.001856 | 0.001797 | 0.001644 | 0.002033 |
| Metal processed during sampling, Mg | 76.12 | 114.71 | 46.21 | 11.83 |

Table 5 lists the pertinent production data during sampling.

The detailed analysis of uncontrolled particulate emissions from pouring is given in Table 6 and that from inoculation in Table 7.

The organic matter adsorbed onto XAD-2 resin was extracted with methylene chloride in the laboratory. The extract was subjected to separation by liquid chromatography with seven solvent systems. The organic matter in each of the seven fractions was determined and then subjected to infrared (IR) spectrophotometry and low resolution mass spectrometry (LRMS). These results gave an approximate weight of each category of organic compounds. The particulate, when obtained, was also extracted for organic content and processed the same way. These results were combined to give the total

*Table 5. Production During Sampling*

| | P | I | C | E | SO | SO[a] |
|---|---|---|---|---|---|---|
| Total metal, Mg | 76.124 | 114.71 | 46.21 | 11.83 | 27.84 | 59.81 |
| Metal/hr, Mg/hr | 18.270 | 28.09 | 11.09 | 2.73 | 10.79 | 10.56 |
| Total sand, Mg | 430.63 | | | | 114.52 | 279.68 |
| Sand/metal ratio | 5.7:1 | | | | 4.47 | 4.99 |
| Coke, Mg | | | 5.78 | | | |
| Coke/metal | | | 1/8 | | | |
| Sample volume, $m^3$ | 27.843 | 26.408 | 24.661 | 29.267 | 15.23 | 26.15 |
| Air flow, $m^3$/Mg processed | 4,392 | 558.7 | 3,407 | 18,900 | 3,516 | 4,865 |
| Sampling time, min | 250 | 245.0 | 250.0 | 240.0 | 155 | 377 |
| Air flow rate, $m^3$/min | 1,337.3 | 261.6 | 629.7 | 860.4 | 631.8 | 562.5 |
| Flask/hr | 294 | 17.6 | | | 250 | 250 |
| Metal/flask, lb | 137 | 3,510 | | | 140-160 | 140-160 |
| Sand/flask, lb | 775 | | | | 750-800 | 750-800 |
| Heats/hr | | | | 0.632 | | |

[a]During test of shakeout scrubber emissions.

*Table 6. Particulate Concentration from Pouring*

| Category | Wt., mg | Load $mg/m^3$ | Percent of Total | Uncontrolled Emission g/Mg |
|---|---|---|---|---|
| < 1 μm | 42.6 | 1.530 | 10.1 | 6.72 |
| 1-3 μm dust | 6.8 | 0.244 | 1.6 | 1.07 |
| 3-10 μm dust | 47.2 | 1.695 | 11.2 | 7.44 |
| > 10 μm dust | 200 | 7.183 | 47.3 | 31.55 |
| Probe rinse | 125.8 | 4.518 | 29.8 | 19.84 |
| Total | 422.4 | 15.171 | 100 | 66.63 |

Sample volume (std): 27.843 $m^3$
Total load: 0.006630 grains/$ft^3$
Metal processed during sample period: 76.124 Mg
Air flow/Mg processed: 4,392 $m^3$

amount of organic compounds. These results have been summarized and presented in Table 8, along with the DMEG values. The DMEG values are the Discharge Multimedia Environmental Goals or the minimum concentration for short-term exposure that has been determined to be detrimental to the environment.[4] Analysis of the results involves obtaining a "concern ratio," which is the emission level divided by the DMEG value. If this is greater than about 10, the category is given more detailed interpretation. In cases of multicomponent compound classes, more detailed interpretation may lower the concern ratio. The DMEG value listed is that value for the single most toxic compound in the entire compound class. Thus, if the organic matter consists of only that compound, an undesirable condition is indicated, but it is also possible for the organic to consist of only the least toxic member of the category, which could be much less toxic. This illustrates the conservative nature of the Level Assessment, giving a certainty of no environmental problem if that is indicated.

Inorganics in the pouring and inoculation particulates were determined by spark source mass spectrometry. This technique was also applied to the XAD-2 resin used in EAF testing. The impinger solutions of the SASS train used for each of the four sources were analyzed for As, Sb, and Hg by atomic adsorption spectrophotometry. These results, except for the cupola, are presented in Table 9. For uncontrolled pouring, the lowest DMEG for the particular element category is exceeded for Cr by a factor > 15. For uncontrolled inoculation, the DMEG is exceeded for: V, Cr, As, and Pb by factors of > 2, 7, > 2, > 1, respectively. For controlled EAF emissions, the DMEG is exceeded for Cr by a factor of 5. The cupola emissions contained 7.66 $\mu g/m^3$ arsenic, 3.8 times the DMEG value.

## DISCUSSION

The results of this study show that there are some areas of concern. A significant finding is the consistent presence of halogenated compounds above the DMEG level. These likely originate by a reaction between the organics present and halogen salts in the flux or furnace lining materials. This is of greater concern if these halogens are fluorocarbons, as could be the case when fluorspar is used as a fluxing agent. However, it would not be unusual for the limestone to contain salt, which

*Table 7. Particulate Concentration from Inoculation*

| Category | Wt., mg | Load $mg/m^3$ | Percent of Total | Uncontrolled Emission g/Mg |
|---|---|---|---|---|
| < 1 μm (filter) | 726.3 | 27.50 | 27.6 | 15.36 |
| 1-3 μm | 1,006.4 | 38.11 | 38.2 | 21.29 |
| 3-10 μm | 376.6 | 14.26 | 14.3 | 7.97 |
| > 10 μm | 523.0 | 19.805 | 19.9 | 11.07 |
| Total | 2,632.3 | 99.68 | 100.0 | 55.69 |

Sample volume (std): 26.408 $m^3$
Total load: 0.04356 grains/$ft^3$
Metal processed during sample period: 114.7 Mg
Air flow/Mg processed: 558.7 $m^3$

*Table 8. Total Organic Emissions from Foundry Processes, Values Given in $mg/mg^3$*

| | Pouring[a] | Inoculation[a] | Cupola[b] | EAF[b] | DMEG |
|---|---|---|---|---|---|
| Aliphatic hydrocarbons | 2.13 | 0.362 | 3.62 | 2.00 | 20 |
| Halogenated hydrocarbons | 2.12* | 0.362* | 3.62* | 2.00* | 0.1 |
| Aromatic hydrocarbons | 1.52* | 0.814 | 3.21* | 1.38* | 1.0 |
| Fused aromatics, >216 MW | c | c | c | c | 0.001 |
| Halogenated aromatics | 1.52* | 0.814* | 3.21* | 1.38* | 0.7 |
| Silicones | 0.19 | 0.205 | 0.81* | 0.15 | 0.7 |
| Heterocyclic O compounds | 1.29 | 0.796 | 1.91 | 0.66 | 300 |
| Nitroaromatics | 0.07 | 0.016 | 0.21 | 0.001 | 1.3 |
| Ethers | 0.53 | 0.213 | 2.07 | 0.01 | 16 |
| Aldehydes | 0.07 | 0.029 | 0.21 | 0.001 | 0.25 |
| Phosphates | 0.16 | 0.033 | 0.31 | 0.33 | 400 |
| Nitriles | 0.07 | 0.016 | 0.21 | 0.001 | 1.8 |
| Heterocyclic N compounds | 0.38* | 0.033 | 0.31* | 0.05 | 0.1 |
| Heterocyclic S compounds | 0.38 | 0.033 | 0.31 | 0.05 | 2 |
| Alcohols | 0.73 | 0.024 | 0.26 | 0.16 | 10 |
| Phenols | 0.12 | 0.024 | 0.26 | 0.05 | 2 |
| Ketones | 1.16 | 0.245 | 2.84 | 0.34 | 12 |
| Amines | 0.85* | 0.024 | 0.26* | 0.16* | 0.1 |
| Alkyl S compounds | 0.21 | 0.024 | 0.26 | 0.05 | 1 |
| Sulfonic acids | 0.17 | 0.024 | 0.26 | 0.05 | 0.8 |
| Sulfoxides | 0.12 | 0.024 | 0.26 | 0.05 | 0.8 |
| Amides | 0.25 | 0.024 | 0.26 | 0.05 | 1.0 |
| Carboxylic acids | 0.73* | 0.024 | 0.26 | 0.16 | 0.3 |
| Esters | 0.60 | 0.067 | 1.68 | 0.05 | 5 |

*DMEG value exceeded.

[a]Before emission control.

[b]After baghouse type emission control.

[c]LRMS indicates possible presence of fused aromatics in all emissions.

*Table 9. Metal Contents of Emissions, Values Given in $\mu g/m^3$*

| Element | Pouring | Inoculation | EAF | Lowest DMEG for Category |
|---|---|---|---|---|
| Li | 0.77 | 8.7 | | $2.5 \times 10^1$ |
| Be | 0.01 | 0.03 | | 2.6 |
| B | 13.05* | >100* | 4.27 | $1 \times 10^4$ |
| F | >15 | | | $2.5 \times 10^3$ |
| Na | >15 | >100 | | $2 \times 10^3$ |
| Mg | >15 | >100 | | $3.2 \times 10^4$ |
| Al | >15 | >100 | | $2 \times 10^3$ |
| Si | >15 | >100 | | $7.5 \times 10^2$ |
| P | >15 | 27 | | $1 \times 10^2$ |
| S | >15 | >100 | | $2 \times 10^4$ |
| K | >15 | >100 | | $2 \times 10^3$ |
| Ca | >15 | >100 | | $5.4 \times 10^2$ |
| Sc | 0.03 | 0.07 | | $5.4 \times 10^3$ |
| Ti | >15 | >100 | | $1 \times 10^4$ |
| V | >15 | >100* | | $5 \times 10^1$ |
| Cr | >15* | 7.1* | 5.12* | 1 |
| Mn | >15 | 62.8 | 3.42 | $5 \times 10^3$ |
| Fe | >15 | >100 | | $1 \times 10^3$ |
| Co | 0.08 | 0.09 | | $4.2 \times 10^1$ |
| Ni | 5.76 | 0.60 | | $1.4 \times 10^1$ |
| Cu | 3.34 | 20.9 | | $2 \times 10^2$ |
| Zn | >15 | >100 | | $5 \times 10^3$ |
| Ga | 0.15 | 2.09 | | $8.3 \times 10^4$ |
| Ge | | 0.10 | | $1.5 \times 10^4$ |
| As | 0.29 | 13.0* | | 2 |
| As** | | 3.69* | ND | 2 |
| Se | 0.17 | 0.8 | | $2 \times 10^2$ |
| Rb | 0.05 | 1.3 | | $3.8 \times 10^4$ |
| Sr | 0.90 | 10 | | $5.6 \times 10^4$ |
| Y | 0.18 | 0.09 | | $1 \times 10^3$ |

continued

could produce chlorinated hydrocarbons, also of concern but to a lesser degree. It appears that clarification of the situation will require more specific analyses combined with a close examination of the raw materials. Installing additional equipment to control the emissions of these compounds could require a large increase in energy consumption as well as capital investment. The better approach would be an examination of raw material sources, their analyses and effect on emissions.

Some interesting observations can be made by comparing the percentage of each organic component present in the four emission sources tested, as presented in Table 10.

The uncontrolled pouring emissions show a distribution of most categories of compounds. This is not unexpected considering the presence of seacoal in the sand.

There was some concern that the uncontrolled inoculation organic emissions might have come primarily from an adjacent pouring line, which could have provided fugitive emissions to the plunging station. This concern is not supported by a comparison of the pouring and inoculation emissions. This is seen by comparing the first two categories, aliphatic hydrocarbons and halogenated hydrocarbons, with the third and fourth categories, aromatic hydrocarbons and halogenated aromatics. The percentages for these two sets are almost completely inverted, and the proportions of other categories likewise do not match well. Thus, the inoculation process itself is indeed a source of organic emissions. This could arise from impurities in the calcium carbide used for desulfurization or the ferrosilicon magnesium inoculant.

Normally it is assumed that organic substances are not present in these materials because of the high temperature of their manufacture; however, as closer environmental examinations are made, unusual discoveries are coming to light. While neither chemists nor metallurgists concern themselves with the thought of organic compound impurities in iron, such a possibility is worth considering. Indeed, it may correlate with some of the "mysteries" of cupola iron versus induction furnace iron. Another data point that suggests the presence of unrecognized factors is the unusual fluidity of cast iron from the experimental gas-fired cupolas. The use of gas for heat and graphite for carbon would certainly reduce the exposure to organic compounds that can be present in coke, not to mention

*Table 9. (continued from previous page)*

| Element | Pouring. | Inoculation | EAF | Lowest DMEG for Category |
|---|---|---|---|---|
| Zr | 0.90 | 4.0 | | 5.1 |
| Nb | 0.12 | | | $2.2 \times 10^4$ |
| Mo | 1.52 | 0.7 | | $5 \times 10^3$ |
| Ag | 0.23 | 1.2 | | $1 \times 10^1$ |
| Cd | 0.18 | 0.2 | | $4 \times 10^1$ |
| Sn | 0.23 | 2.5 | | $1 \times 10^2$ |
| Sb | 0.17 | 21.9 | 0.16 | $5 \times 10^2$ |
| Te | 0.05 | 0.2 | | $2.2 \times 10^2$ |
| Cs | 0.00 | 0.09 | | $2 \times 10^3$ |
| Ba | 14.87 | >100 | | $5 \times 10^2$ |
| La | 0.58 | 1.3 | | $1.1 \times 10^5$ |
| Ce | 0.71 | 9.1 | | $1.3 \times 10^5$ |
| Pr | 0.03 | | | $1.2 \times 10^5$ |
| Nd | 0.03 | | | $9.6 \times 10^4$ |
| Sm | 0.05 | | | $1.1 \times 10^5$ |
| Eu | 0.01 | | | $1.3 \times 10^5$ |
| W | 0.03 | | | $1 \times 10^3$ |
| Hg** | 2.53 | 3.07 | 1.90 | $5 \times 10^1$ |
| Pb | 2.58 | >100* | 17.1 | $1 \times 10^2$ |
| Bi | 0.02 | 0.5 | | ? |
| Th | 0.24 | | | $5.3 \times 10^4$ |
| U | 0.08 | | | $1.5 \times 10^1$ |

*DMEG exceeded.
** Analysis by atomic absorption of impinger solutions.
ND = Not detected.
Blanks indicate the element did not exceed the blank.

the trace inorganics. If organic compounds are present in the iron, they likely would segregate at the grain boundaries, which is metallurgically significant. If any organic molecules were trapped in the iron grains (crystals), their interaction with dislocations would certainly be different from that of carbon atoms, and thus some difference in mechanical properties would be obtained. The indicated presence of organics in the inoculation process thus signals an area of research that could have metallurgical as well as environmental consequences. The analysis of the basic and secondary raw materials would be a good starting point to pursue this, if the presence of organic compounds in the metal can be verified.

The presence of organic compounds in the cupola offgas is not surprising, even though afterburners are used to eliminate carbon monoxide and organic compounds.

Only a few elements exceed the DMEG (see Table 9) for any of the processes studied. None of the elements exceed the DMEG by large (i. e., > 100) ratios. This does not mean, however, that these emissions should be ignored. It may be possible to achieve a partial reduction in these emissions by determining in which raw material they occur. For example, arsenic, which exceeded the DMEG for inoculation and cupola melting, may originate in the ferrosilicon, calcium carbide, coke or fluxes used in these processes. A material specification change might significantly reduce arsenic emissions.

Chromium exceeded the DMEG for all processes except the cupola. Halogen salts contained in the raw materials may leach out small amounts of the contained chromium as the volatile halide. Here again an examination of the purity of the raw materials could lead to a partial solution to the problem.

A significant finding is the small amount of fused aromatics from the pouring line. In the previous study[2] the shakeout was studied because the work of Bates and Scott[1] showed it produced the greatest quantity of emissions. Their work was a laboratory study which collected emissions from a small sealed flask. In the laboratory, pouring emissions were only slightly less than the shakeout emissions. The actual plant emissions collected from the shakeout showed a lack of significant or even measurable PNAs of health concern. It was hypothesized[2] that by the shakeout stage the high boiling PNAs (496 to 510C for BaP) were condensed onto the sand or adsorbed onto the clay and were not significantly released on shakeout. Most of the high molecular weight shakeout emissions were naphthalene derivatives. This led to the selection of the pouring process as the most likely place to find PNAs in the casting process because the temperatures obtained are certainly high enough to boil off these compounds. There remains the speculation that some of the emissions from pouring would be oxidized by the burning of methane, hydrogen, and carbon monoxide, the major pouring emissions. The finding of very little fused aromatics from the pouring process seems to confirm that most of the high molecular weight compounds are destroyed rather than emitted to the atmosphere during pouring. Since health statistics show a slightly higher rate of cancer

*Table 10. Percentage of Each Component in Samples*

| Category | Uncontrolled P | Uncontrolled I | Controlled C | Controlled E |
|---|---|---|---|---|
| Aliphatic hydrocarbons | 13.9 | 8.5 | 13.6 | 21.9 |
| Halogenated hydrocarbons | 13.8* | 8.5* | 13.6* | 21.9* |
| Aromatic hydrocarbons | 9.9* | 19.1 | 12.1* | 15.2* |
| Halogenated aromatics | 9.9* | 19.1* | 12.1* | 15.2* |
| Silicones | 1.2 | 4.8 | 3.0* | 1.6 |
| Heterocyclic O compounds | 8.4 | 18.7 | 7.2 | 7.3 |
| Nitroaromatics | 0.5 | 0.4 | 0.8 | 0.01 |
| Ethers | 3.5 | 5.5 | 7.8 | 0.1 |
| Aldehydes | 0.5 | 0.7 | 0.8 | 0.01 |
| Phosphates | 1.0 | 0.8 | 1.2 | 3.7 |
| Nitriles | 0.5 | 0.4 | 0.8 | 0.01 |
| Heterocyclic N compounds | 2.5* | 0.8 | 1.2* | 0.5 |
| Heterocyclic S compounds | 2.5 | 0.8 | 1.2 | 0.5 |
| Alcohols | 4.7 | 0.6 | 1.0 | 1.8 |
| Phenols | 0.8 | 0.6 | 1.0 | 0.5 |
| Ketones | 7.5 | 5.8 | 10.7* | 3.7* |
| Amines | 5.5* | 0.6 | 1.0* | 1.8* |
| Alkyl S compounds | 1.4 | 0.6 | 1.0 | 0.5 |
| Sulfonic acids | 1.1 | 0.6 | 1.0 | 0.5 |
| Sulfoxides | 0.8 | 0.6 | 1.0 | 0.5 |
| Amides | 1.6 | 0.6 | 1.0 | 0.5 |
| Carboxylic acids | 4.7* | 0.6 | 1.0 | 1.8 |
| Esters | 3.9 | 1.6 | 6.3 | 0.5 |
| Total $mg/m^3$ | 15.37 | 4.25 | 26.55 | 9.10 |

*DMEG was exceeded.

only among workers in the pouring-cooling area,[5] this leaves cooling as the remaining process where a problem might be found.

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