Hazardous Waste Research and Information Center
One East Hazelwood Drive
Champaign, Illinois 61820

HWRIC TR-011

Waste Management Study of Foundries Major Waste Streams: Phase I

by

Daniel L. Twarog
American Foundrymen's Society, Inc.
and
University of Alabama

ENR
Illinois Department of Energy and Natural Resources

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Prepared by

Daniel L. Twarog
American Foundrymen's Society, Inc.
Des Plaines, Illinois

and

Department of Chemical Engineering
University of Alabama

Prepared for

The Illinois Hazardous Waste Research
and Information Center
One East Hazelwood Drive
Champaign, Illinois 61820

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Front cover:
From 2 to 3 cu. yards of dust and fume arising daily at 11 dust-producing points in the sand handling operations -- shakeout, conveyors and muller -- at Bay City Steel Castings Div. of American Hoist & Derrick Company are trapped in a Wheelabrator Turbex wet collector.

WASTE MANAGEMENT STUDY OF FOUNDRIES MAJOR WASTE STREAMS

PHASE I

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ABSTRACT

Research on emission control and waste disposal is the number one priority within AFS. In an industry survey conducted by AFS, ten top areas of concern were outlined, headed by sand system waste and emissions from molding, pouring, melting and shakeout in iron and steel green sand foundries. The objective of the present program is to define the foundry waste streams and emissions, establish where the streams originate, and their make-up. Currently available technology will then be identified to minimize, treat, dispose, or reuse the waste. Information obtained will be summarized into a manual for use by foundry operators. Additional research and development needed to respond to environmental regulations will be identified. A primary driving force for this work is the Clean Air Act Amendments of 1990 which will set new regulations for air emissions from foundries for 189 hazardous air pollutants (HAP) by 1997.

This report covers the first year's research on the nature of the foundry waste streams in the form of air emissions from processes of coremaking, molding, pouring, and shakeout and establishes where they originate, and their makeup. Binder chemicals are a major potential contributor to emissions from coremaking and subsequent processes. Remaining objectives will be accomplished in a further development of the program.

The approach used includes a review of all available information. Sources were the technical literature, suppliers of chemicals to foundries, AFS workshops, USEPA Office of Air Quality Planning and Standards, technical meetings, and visits to foundries.

The data in the literature on organic HAP relate to workplace health and safety data which identify chemical types and concentrations, and emissions during pouring and cooling. There are no significant variations of temperature, metal composition, and metal to sand ratio to allow extrapolation to different systems. It is apparent that additional research is needed to determine the important parameters that control HAP emissions.

Information from suppliers and other sources was combined with data from the literature to identify 16 HAP non-metal chemicals potentially present in air emissions from foundries. In addition, HAP from specific binder systems are also defined.

The next phase of this program will identify currently available technology to minimize, treat, dispose, or reuse the waste. Information obtained will be summarized into a manual for use by foundry operators.

WASTE MANAGEMENT STUDY OF FOUNDRIES MAJOR WASTE STREAMS
PHASE I

BACKGROUND

Metalcasting is one of the most recycle-intensive of all manufacturing industries. Nevertheless, it produces solid, liquid, and volatile wastes. As a result, many of the environmental regulations which have been issued have a substantial impact on the foundry industry. In attempting to comply with these regulations, the industry has seen its costs rise, particularly in comparison with competitors in countries where environmental regulations are less stringent. Indeed, some organizations have found it expedient to move their operations overseas rather than comply with increasingly stringent U. S. environmental laws. Because the foundry industry must meet environmental requirements of the United States and compete internationally, it is in need of a significant effort to develop cost effective technology which will allow it to meet United States environmental regulations.

More stringent environmental emission limits and limits on concentrations of hazardous materials in the workplace make dealing with environmental problems a major expense that is rising each year. In 1989, over 2 percent of the production costs of a casting were a result of compliance and waste disposal costs. For foundries that cast leaded copper-base alloys this amounted to 9 percent. Environmental legislation recently enacted is expected to double the compliance and waste disposal costs by 1993 (3). New environmental regulations regarding sand disposal in landfills will significantly increase landfill complexity and costs. The National Pollutant Discharge Elimination System requires permits for storm water discharges. There are also new regulations for underground storage tanks, underground pipelines, and for sludge disposal.

While the regulations mentioned above are important, the Clean Air Act Amendment of 1990 will have the most far-reaching impact on the nation of any recent new environmental legislation. The original Clean Air Act failed to address toxic air emissions in any meaningful way, and EPA promulgated rules for only a few pollutants. The amendments, however, cover 189 air toxics, and Maximum Achievable Control Technology (MACT) standards will be applied to source categories which emit 10 tons annually of a single toxic or 25 tons per year of a combination of air toxics. The goal is to have all toxic emissions regulated within ten years (5,6). The EPA schedule calls for iron and steel foundry air emission standards to be in place by 1997.

The American Foundrymen's Society (AFS) asked each of the eleven divisions of AFS to have their technical committees identify and prioritize the research needs of the U. S. foundry industry. The recommendations were categorized in two areas: materials and processes. The four process categories were green sand, chemically bound, investment casting, and expendable pattern (Figure 1). In each case, waste identification was a common element, in three of the four areas waste treatment or recycling of waste was listed, and two listed identification of emissions as a priority. The present effort is directed toward the identification and categorization of the origin of waste streams and emissions in the metalcasting industry.

Research on emission control and waste disposal is the number one priority within AFS. The identification of foundry process waste is the first step in developing specific research programs. To this end, AFS conducted an industry survey to determine the top ten foundry waste streams of environmental concern. A copy of the survey document is attached as Figure 2. The top ten areas of environmental control concern to American foundries identified from this survey are given below (in priority order).

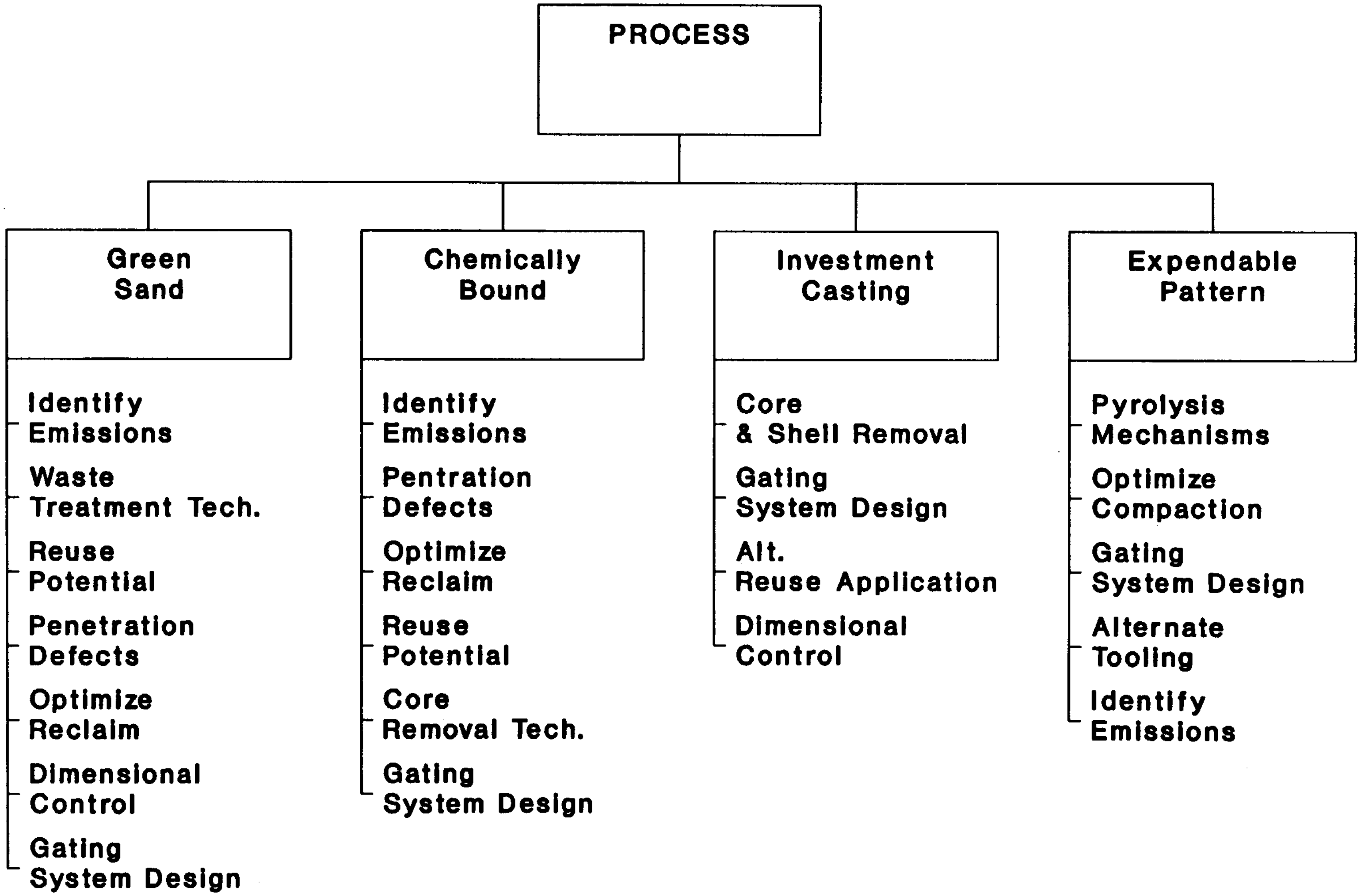
1. Sand System Waste
2. Mold and Pouring Emissions
3. Melt Furnace Emissions
4. Shake-Out Emissions
5. Storm Water Runoff
6. Unfired Core Waste
7. Core Room Emissions
8. Cleaning Room Dust
9. Shotblast Dust
10. Emission Control Water

Leading the list is sand system waste. Only recently, as landfills have begun to close down, has the issue of the disposal of spent molding sand been recognized as being a serious problem.

The second area is mold and pouring emissions, many of which come from resin binders in the sand and cores. (Note the importance of core binders as contributors to the waste problems in the top-ten list.) An idea of the complexity of the airborne emission problem from resin binders can be judged from the fact that there are some nineteen different <u>families</u> of resin binder systems in commercial use in foundries today (7). The airborne products given off when these systems are used to make cores or molds, and when they break down on exposure to molten metal, depend on the temperatures to which the resins are exposed, and on process operating conditions. Important parameters are the pressures generated,

Figure 1

Foundry Research Needs



- PROCESS
  - Green Sand
    - Identify Emissions
    - Waste Treatment Tech.
    - Reuse Potential
    - Penetration Defects
    - Optimize Reclaim
    - Dimensional Control
    - Gating System Design
  - Chemically Bound
    - Identify Emissions
    - Pentration Defects
    - Optimize Reclaim
    - Reuse Potential
    - Core Removal Tech.
    - Gating System Design
  - Investment Casting
    - Core & Shell Removal
    - Gating System Design
    - Alt. Reuse Application
    - Dimensional Control
  - Expendable Pattern
    - Pyrolysis Mechanisms
    - Optimize Compaction
    - Gating System Design
    - Alternate Tooling
    - Identify Emissions

Source: AFS Research - 1992

Name ______________________________

Company ____________________________

A. Choose the top 10 areas, in descending order, of major concern to your company.

___Sand System Waste
___Shotblast Dust
___Cleaning Room Dust
___Spent Furnace Refractory
___Sand Reclaim Dust
___Crucibles/Ladles
___Slags/Dross
___Floor Sweepings
___Unfired Core Waste
___Fired Core Waste
___General Refuse
___Off-spec. Material
___Spent Packaging/
Containers
___Scrap Polystyrene

___Cooling Water (contact)
___Cooling Water
(noncontact)
___Emission Control Water
___Cutting Oils
___Storm Water Runoff
___Cleaning Water
___Solvents
___Off-spec. Binders
___Scrubbing Solutions
___EPC Pattern Coating and
Adhesives

___Melt Furnace Emissions
___Ladle Emissions
___Sand Reclaim Emissions
___Core Room Emissions
___Mold and Pouring
Emissions
___Shake Out Emissions
___Sand Transport and
Cooling Emissions
___Molding Line Emissions
___Welding and Cutting
Emissions
___Cleaning Room Emissions

___General Refuse
___Off-spec. Material
___Spent Packaging/
Containers
___Scrap Polystyrene and
PMMA Patterns

___PCBs
___Furnace Dust
___Hazardous System Sand
Waste

B. List any additional categories which may require consideration.

____

____

____

C. If specific subcategories can be identified, please include (i.e., CaC_2 desulfurization slag is a subcategory of dross/slag).

____

____

____

D. Do you foresee the top 10 categories changing priority over the next three to five

years? ____

If so, how might they change? ______________________________________

____

____

FIGURE 2. - AFS SURVEY OF FOUNDRY WASTE STREAMS

and other gas species present, such as atmospheric moisture. No systematic study has been published which defines what these reaction products are, or how to control them.

Another notable item on the list is melt furnace emissions, which are receiving increased attention. Shakeout area emissions are related to the pouring emissions and binder systems, and are increasingly recognized as a problem to be addressed. While stormwater runoff has been largely ignored, the new storm water regulations mentioned above have attracted a lot of industry attention.

The list of top-ten areas of environmental concern show a recognition that elimination or control of air emissions in foundries will necessarily require a high level of attention. The Clean Air Act Amendments of 1990 (CAAA) will require this. In the top-ten list, only sand system waste and unfired core waste are not related in some way to air emissions. Dust emissions have received attention in the past, and technology for dealing with them is readily available. Emissions from the melt furnaces, however, have not been dealt with so extensively, and increased attention will be required. By far the largest problem in air emissions is related to air toxics, which are primarily organic compounds emitted during core making, pouring, and shake-out. The nature and amount of these airborne toxics are largely unknown, as are the methods for controlling the emissions. The need for emphasis on addressing air emissions is clear.

There are a number of strategies for dealing with foundry waste. Clearly, minimization of the waste generated is the first step. Elimination of those processes and products which inherently produce toxic wastes and emissions, or substitution of more benign processes and materials is a further step. Some binder systems which reduce environmental problems are now on the market. Increased use of reclamation and recycling of waste products will be important. Conversion of waste to useful commercial products at the foundry site is another tactic. For the remainder of the waste generated, however, it will be necessary to develop treatment methods which are inexpensive and reliable.

AFS has developed a research plan to address environmental concerns of the metalcasting industry. The research plan outlined by AFS is given in Figure 3. The objective of the program is to define the foundry waste streams and emissions, establish where the streams originate, what they consist of, and then to identify current available technology to minimize, treat, dispose, or reuse the waste. The information obtained will be summarized into a manual for use by foundry operators. Additional research and development needed to respond to environmental regulations will be identified.

The first step in this process is to define the foundry waste streams that pose the largest problems. This first phase has already been completed, and the results were given above. The industry survey

Figure 3

ENVIRONMENTAL RESEARCH PLAN BY PHASE

- Phase One - Conduct Industry Survey to Assess the Top 10 Foundry Waste Streams
- Phase Two - Subcategorize Each Stream with Their Specific Input Streams
- Phase Three - Characterize Each Input Stream from Existing Knowledge Base
- Phase Four - Identify Available Technology to Treat, Dispose, or Reuse Input Streams
- Phase Five - Prioritize Required Research & Development Towards Additional Technologies
- Phase Six - Publish a Manual which Details the Results

2/28/91

identified the ten waste streams of most concern to the industry. Interestingly, there was little disagreement among the foundries which responded as to the importance of these specific waste streams.

The second step is to define the nature of the foundry waste streams, establish where the streams originate, and what they consist of. This report covers the first year's research on this aspect of the emission studies.

The further development of the program will identify current available technology to minimize and treat, or dispose, or reuse the waste, and to define additional research and development needed to respond to environmental regulations. A manual summarizing the current knowledge base will be issued at the end of the program.

APPROACH

Up to now, foundry waste emission concerns have emphasized sand, water, and particulate emissions. Concerns about emissions of air toxics have largely been focused on occupational health and safety. The Clean Air Act Amendments of 1990 (CAAA) require the control of emissions of toxic and hazardous materials to the air. The scope of a project which dealt with all types of emissions from foundries would be far too large for the current project. Therefore, this project dealt only with air emissions of toxic and hazardous chemicals.

The U. S. foundry industry is very diverse. A comprehensive study of air emissions from all the different types of foundries and binder systems is beyond the scope possible for this project. Figures 4 and 5 show that grey iron, ductile iron and steel accounted for about 84 percent of the metal cast in 1990. In addition, EPA has chosen iron and steel foundries to be the first foundry types to come under compliance of the CAAA. Therefore, the emphasis for this project was air emissions from green sand iron and steel foundries. In particular, emphasis has been placed on core making, pouring, and shake-out. Metal preparation and melting have not been considered, as there are a number of current technologies for treating melting effluents (such as baghouses, etc.).

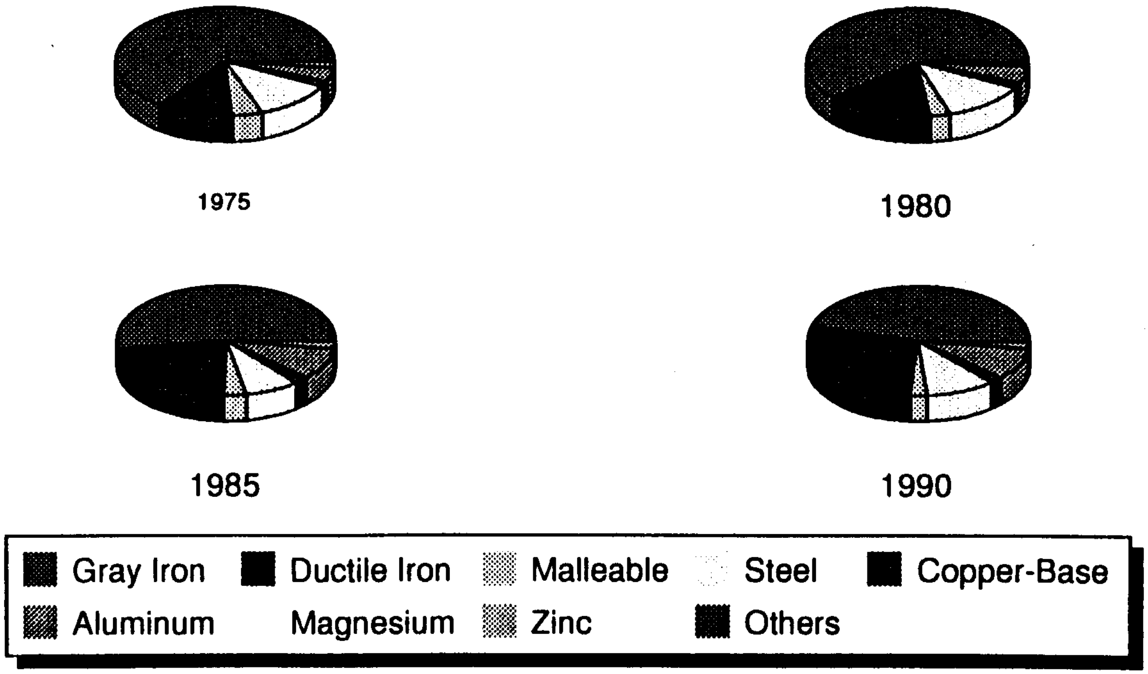
The approach being used includes a review of available information on emissions. The information sources were the technical literature, suppliers of chemicals to foundries, AFS workshops, technical meetings, and visits to foundries. A questionnaire was developed in the early stages of the project but has not been widely distributed. This is mainly because of attempts to coordinate this project with EPA's efforts.

Figure 4

FOUNDRY WASTE MANAGEMENT PROJECT

TONS OF METAL CAST

United States and Canada



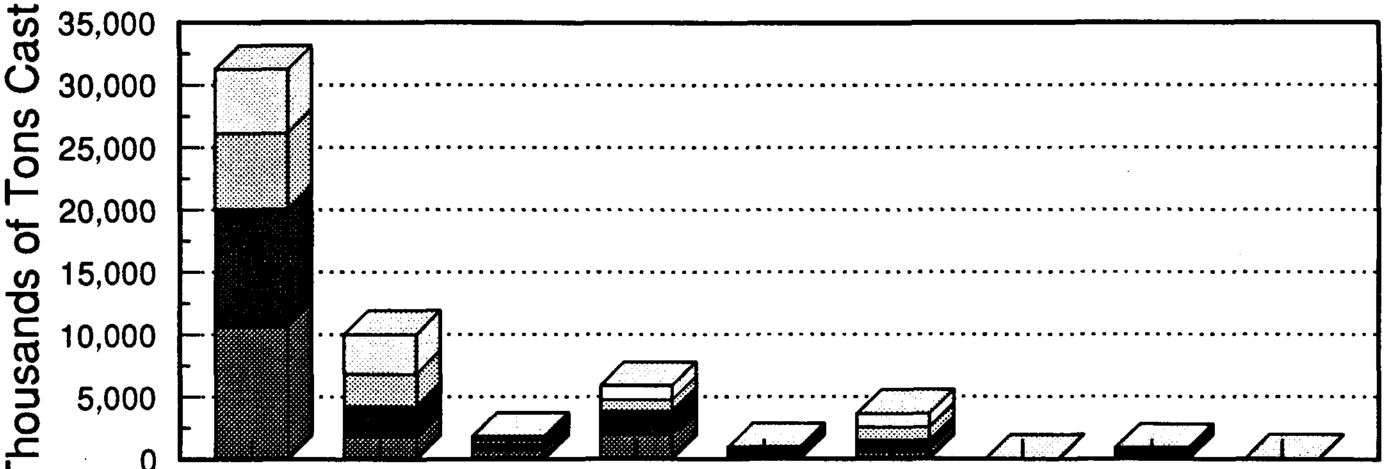
Source: Metal Casting Industry Census Guide
April, 1992

Figure 5

FOUNDRY WASTE MANAGEMENT PROJECT

TRENDS IN TONS OF METAL CAST

United States



Year		Gray Iron	Ductile Iron	Malleable	Steel	Copper-Base	Aluminum	Magnesium	Zinc	Others
1975	▩	10,622	1,824	731	1,938	256	688	16	286	18
1980	■	9,399	2,400	450	1,878	244	769	12	172	17
1985	▒	6,093	2,608	376	940	235	1,114	12	255	23
1990	░	5,120	3,190	276	1,136	216	1,067	14	208	31

Source: Metal Casting Industry Census Guide
April, 1992

LITERATURE REVIEW

A review of the literature for emissions from foundries has focused on binder systems, pyrolysis and thermal decomposition products of binder systems, and air toxics. Binder systems are considered to be the most likely source for the emission of the chemicals on EPA's list of Hazardous Air Pollutants (HAP). The binder starting materials and pyrolysis products all present a potential HAP release. There are very few literature articles on emissions from these binder systems.

SEARCH METHODOLOGY

Several different approaches were used in order to search for relevant information. They were the following:

Database of STN International

This major database contains references to most of the scientific and technical literature. Included in the database are Chemical Abstracts, Engineering Index, Government Documents and Patents, both U.S. and foreign work, and foreign language articles as well as English. The search was performed with emphasis on the following keywords: pyrolysis, thermal decomposition, and the specific chemical name (phenol, formaldehyde, etc.).

National Technical Information Service (NTIS)

This database contains U. S. Government Documents. The University has 1980-1989 on CD-ROM in the Engineering Library. Several Articles were found of interest. The references from these articles provided several more sources.

Database of the AFS Library

A search was performed on this database with the assistance of an AFS librarian. This search proved to be very useful in providing articles of interest, which were retrieved from various sources through interlibrary loan and the help of AFS.

Compendex Plus

This database is the CD-ROM equivalent of the Engineering Index. The Engineering Library contains the years 1987-1991 on CD-ROM.

The University of Alabama Library

The University of Alabama is a member of the Association of Research Libraries and has extensive holdings. The holdings are computerized so that it can be searched for books and journal titles by author, subject, or Library of Congress call number.

These searches led to 26 articles and journals that were relevant to this project. The articles and journals are listed in the bibliography at the end of this report.

BINDER PROCESSES AND POTENTIAL EMISSIONS

The primary driving force behind this project is the new Clean Air Act Amendments of 1990 (CAAA) (24). This legislation requires more stringent control of the emission of the 189 hazardous air pollutants listed under Title III of the CAAA. One of the main sources for these HAPs from foundries are the binders used in core and mold production. Although not counted as a resin binder, green sand may be another source. All of these sources are discussed below with their potential emissions.

There are three main classes of binder systems: heat activated, no bake, and cold box (22). The heat activated class includes several different binder systems. Among these are the hot box, shell, warm box, and core oil.

Hot Box

This process is initiated by blowing a resin and a sand mixture into a heated corebox (2,22). The curing process begins immediately upon contact with the heated corebox (1,22). Operating temperatures of the box are in the range of 450-550 °F. Emissions occur during the baking of the core and when the core is removed from the box (2).

Binders that are in the hot box category include phenolic resins, furan resins, and combinations of the two. These resins can also be modified by the addition of urea. The phenolic resins are phenol formaldehyde polymers. Sometimes urea formaldehyde is added in order to improve the tensile strength. The furan resins are mixtures of furfuryl alcohol and urea formaldehyde polymers.

The chemical reaction for the phenolic resin of this process involves reacting phenol with an excess of formaldehyde and an aqueous weak acid (usually ammonium chloride) (1). The acid provides the hydrogen ions which catalyze the reaction. The resin is allowed to polymerize until the reaction is stopped, still in the liquid state.

The cure time of the resin binding the sand is a function of the temperature of the corebox and the catalyst type (8). The reaction is an exothermic reaction, therefore, the resin continues to cure even after it is removed from the corebox. Hot box binders have a high hot strength and fewer shakeout problems than other binders.

Hot-box binders decompose during the casting process and emit possible pollutants covered by the CAAA. Formaldehyde is a concern because it is present in excess (1,2). Table 1 is a list of possible HAP emissions covered by the CAAA when pouring metal in molds made by the hot box process (2,8,9,21,23).

Table 1. Potential HAP Emissions from Hot Box Binders.

Phenols
m-Xylene
Benzene
Aniline
Hydrogen cyanide
Acetaldehyde

Formaldehyde
o-Xylene
Toluene
Napthalene
Acrolein
Hydrogen sulfide

The laboratory experiments performed by Scott et al. yielded information on the amounts of chemicals released during the pouring and cooling process (23). They obtained emissions data for 12 systems: green sand, dry sand, silicate-ester, core oil, alkyd isocyanate, phenolic urethane, phenolic no-bake, low N_2 furan-H_3PO_4, medium N_2 furan TSA, furan hot box, phenolic hot box, and shell (phenolic). The test method used in their laboratory experiments was the quasi-stack method. The hot-box test molds were prepared using an irregular gear pattern designed by AFS Committee 80F. The gear casting with the gating system and riser weighed about 40 Kg and was poured in a mold weighing appoximately 100 Kg. The castings were poured with a gray iron at 2642 °F. The concentrations were measured in a constant 1000 L/min flow of gas through the stack. The sand-resin mixture was cured against a heated pattern and then baked to ensure proper curing. Table 2 lists the results from their hot-box experiments.

Shell

As with the hot box process, the shell process begins with the addition of heat (22). The sand used in the shell process is usually precoated before arriving at the foundry (8,9). Therefore, the core making process can be broken down into five steps: blow, invert, drain, cure, and strip (22). The operating temperature of the corebox is above 450 °F. The heat transfer must be uniform in order to ensure proper binding of the sand.

The chemistry of the shell process involves the reaction of formaldehyde, an excess amount of phenol, and an acid catalyst (1). This reaction yields a strong three dimensional polymer network which is then either solvent coated or heat coated with hexamine. Hexamine is the cross linking agent which carries the reaction to completion upon the addition of heat. The cure speed is a function of time and temperature (8). Some of the advantages of the shell process include indefinite shelf life and the applicability to a wide range of metals.

Table 2. Quantities of Chemicals Released in the Hot Box Process.

Chemical	Concentration (mg/m^3) from Hot Box Binders	
	Furan Hot Box	Phenolic Hot Box
Sulfur dioxide	2.8	1.2
Hydrogen sulfide	1.9	0.3
Hydrogen cyanide	110.0	39.0
Ammonia	620.0	360.0
Nitrous oxides	13.0	21.0
Formaldehyde	0.3	0.2
Acrolein	0.4	0.3
Total Aldehydes	<5	9
Total Aromatic Amines	96	42
Benzene	17	33
Toluene	<1	6
m-Xylene	<1	4
o-Xylene	<1	<1
Napthalene	<1	<1
Phenol	0.5	6.7
Bischloromethyl ether	<10 ppb	<10 ppb

Unlike the hot box, the shell process is rich in phenol (1). Therefore, a major concern environmentally, is the emission of phenol. Table 3 lists possible emissions covered by the CAAA when pouring metal into molds made by the shell process (1,2,9,11).

Table 3. Possible HAP Emissions from Shell Binders.

Phenol
Aniline
Toluene
o-Xylene
Napthalene
Acetaldehyde
Formaldehyde
Benzene
m-Xylene
N,N dimethyl formide
Acrolein
Hydrogen sulfide

In their laboratory study, Scott et al have reported the amounts of chemicals released from shell process molds during the pouring and cooling process (23). The data obtained are shown in Table 4.

Table 4. Quantities of Chemicals Released in the Shell Process.

Chemical	Concentration (mg/m^3)
Sulfur dioxide	30.0
Hydrogen sulfide	0.8
Hydrogen cyanide	90.0
Ammonia	33.0
Nitrous oxides	8.5
Formaldehyde	0.3
Acrolein	0.4
Total Aldehydes	<5
Total Aromatic Amines	20
Benzene	57
Toluene	24
m-Xylene	5
o-Xylene	<1
Napthalene	<<1
Phenol	21.0
Bischloromethyl ether	<10 ppb

Moorman et al have reported on the emissions of chemicals from cooling molds in operating foundries (17). They obtained emission data for four different binder systems: furan (urea-formaldehyde-furfuryl alcohol), green sand with sea coal, urethane (phenolic isocyanate), and phenol-formaldehyde resins in shell molds. The emissions were collected using a train of three components: cyclone, venturi scrubber, and an entrainment separator. Particles were collected in the range of 0.5-10 µm in diameter. Air entered the cyclone at 100 cfm. The water soluble fraction and particulate fraction were collected and analyzed. Emissions of polycyclic aromatic hydrocarbons and phenols were obtained from areas where shell-sand castings were cooling. Table 5 gives the results for these shell mold tests.

Laboratory work was performed by Emory et al to quantitate potentially hazardous nitrogen-containing compounds in foundry mold effluents (11). When metal pouring was started, sampling was begun and continued for 30 minutes while the casting solidified and cooled. The binder systems studied included an alkyd isocyanate, a phenolic urethane, a shell binder, a phenolic no-bake, a nitrogen free furan no-bake, and a furan no-bake. Using an experimental procedure similar to that used by Scott et al (23), they employed the quasi-stack method to collect emissions while the mold was cooling. A constant flow rate of 1000 L/min was maintained through the chimney of the hood. The pouring temperature was 2650 °F and new sand was used. Their results for shell molds can be found in Table 6.

Table 5. Emissions from Shell Molds.

Particulate Fraction

Compound	Emission (μg/g particulate)
Acridine	<0.6
Napthalene	<0.6
Carbazole	<0.6
Phenanthrene	1500
Benzo(a)anthracene \	350
Chrysene /	
Benzo(a)pyrene	270
Dibenzo(a,h)anthracene	<0.6

Water Soluble Fraction

Compound	Emission (μg/g sample)
Phenol	1600
Pentachlorphenol	<2
4-Nitrophenol	1800
2-Nitrophenol	2300
2,4-Dimethylphenol	60

Table 6. Amines Present in Shell Mold Effluent.

Compound	Concentration (mg/m^3)
Aniline	3.1
Triethylamine	<0.2
Morpholine	<0.2
N,N dimethylformamide	0.3
N,N dimethylaniline	<0.2
o-Toluidine	<0.2
2,4-Xylidine	<0.2
o-Anisidine	<0.2
p-Anisidine	<0.2
Mesidine	<0.2

Warm Box

The warm box process uses the same process steps as the hot box but the binders are cured at a lower temperature (22). The temperature range for this process is 300-450 °F, with the optimum temperature being 400 °F. This is approximately 100 degrees below that of the hot box.

The ability to cure at low temperatures is due to the catalyst used in the process (8). The catalyst is copper salts or sulfonic acids. These catalysts dissociate quickly at low temperatures and rapidly cure the cores at low heat. The cure speed can be controlled by the different formulations of the catalyst. Advantages of the warm box are the lower energy cost, a longer bench life, and low gas evolution (8,15). They can also be used with a wide variety of metals (8).

As with the hot box, the warm box binders are phenolic resins and furan resins (8). The furan resin is high in furfuryl alcohol but low in nitrogen and free formaldehyde. These binders can also be modified with the addition of urea formaldehyde or phenolic formaldehyde. Metal pouring with molds made by the warm box process may release the HAP's phenol and formaldehyde (20,21).

Core Oil

This process involves the mixing of core oil and a water activated cereal (22). This mixture is blended with sand and then blown into the core box at room temperature. The wet core is then removed and placed into a oven for curing. The catalyst for this reaction is heat. The final strength of the core is a function of oven temperature, drying humidity, and time. Table 7 shows the possible HAP emissions when pouring metal into cores made by this process (23). Chemicals released during this process have been quantified by Scott et al. (23) (Table 8)

Table 7. Possible HAP Emissions from Core Oils.

Phenol
Benzene
m-Xylene
Napthalene
Hydrogen cyanide
Amines (Aniline)
Formaldehyde
Toluene
o-Xylene
Acrolein
Acetaldehyde
Hydrogen sulfide

Table 8. Quantities of Chemicals Released in the Core Oil Process.

Chemical	Concentration (mg/m^3)
Sulfur dioxide	2.4
Hydrogen sulfide	1.2
Hydrogen cyanide	1.8
Ammonia	0.8
Nitrous oxides	1.7
Formaldehyde	2.0
Acrolein	1.6
Total Aldehydes	16
Total Aromatic Amines	2
Benzene	49
Toluene	10
m-Xylene	5
o-Xylene	6
Napthalene	<1
Phenol	1.2

No Bake

The second group of binders are the no bake (self-setting) binders, which are either acid catalyzed or ester cured (1,2,8,22). The difference between these binders and the ones previously mentioned is that they cure at room temperature. Heat is not required in the process. The operating temperatures for this process range from 75-85 °F (22). The sand, binder, and catalyst are continuously mixed and blown into the corebox. For the best results, the sand mixture should be used in a relatively short time after the mixing of the resin and sand.

The chemistry of the phenolic no-bake binder consists of copolymers of formaldehyde with phenol and/or urea containing varying amounts of furfuryl alcohol (2). The formaldehyde is fed at excess during the reaction. The acid catalyst is an organic sulfonic or phosphoric acid, with the organic usually being benzene or toluene (1,8). The acid provides the hydrogen ions to catalyze the reaction (1). The strong acid lowers the activation energy of the binder allowing it to cure at room temperature. The curing time depends on the type of resin, sand chemistry, percent and type of catalyst, and temperature (22).

The binders used in this process include furan/acid, phenolic/acid, phenolic/ester, silicate/ester, phenolic urethane, and alkyd urethane systems (1,2,8,9,22). Once again, modifications can be made to these binders. The furan/acid system consists of furfuryl alcohol and the catalyst (8). Other chemicals such as urea, formaldehyde, and phenol may be incorporated into the resin along with the furfuryl alcohol. The phenolic/acid system consists of phenol and formaldehyde. The phenolic/ester system contains a phenolic resole, an alkaline catalyzed thermosetting phenol-formaldehyde type resin consisting primarily of partially condensed phenol alcohols, and an ester. The ester causes the resole to polymerize into the binder and also yielding polymerized phenol formaldehyde resin, a metallic salt, and an alcohol as byproducts. The silicate/ester system contains a sodium silicate solution and an ester. The phenolic urethane system is made with formaldehyde, phenol, xylene, cumene, 1,2,4 trimethylbenzene, methlene phenylene isocyanate, and napthalene (20). The alkyd urethane is composed of lead, cobalt, napthalene, 1,2,4 trimethylbenzene, and methylene phenylene isocyanate. All these binders are potentially sources of HAPs. Table 9 shows possible HAP emissions when metal pouring into molds from the no-bake systems (1,2,11,13,23). Specific quantities of chemical species as reported by Scott et al. are given in Table 10 (23).

Table 9. Possible HAP Emissions from No-Bake Binders.

Phenols
Carbonyl sulfide
Methyl ethyl ketone
Toluene
Cresol
Napthalene
Acetaldehyde
Hydrogen Sulfide
Formaldehyde
Carbon disulfide
Benzene
Xylenes
Aniline
Acrolein
Hydrogen cyanide

Table 10. Quantities of Chemicals Released in the No-Bake Process.

Chemical	Concentration (mg/m^3) by Binder Systems				
	Alkyd Isocyanate	Phenolic Urethane	Phenolic No-Bake	Low N_2 Furan-H_3PO_4	Med N_2 Furan-TSA
Sulfur dioxide	1.1	1.4	310.0	15.0	120.0
Hydrogen sulfide	0.2	1.3	30.0	10.0	12.0
Hydrogen cyanide	4.8	24.0	0.6	9.1	15.0
Ammonia	1.0	1.9	0.8	1.0	5.0
Nitrous oxides	9.7	1.0	0.6	0.3	7.7
Formaldehyde	2.9	0.5	0.2	6.6	1.6
Acrolein	2.4	0.7	0.1	0.7	0.4
Total Aldehydes	59.0	<5	63.0	6	420
Total Aromatic Amines	<1	8	<1	2	9
Benzene	146	122	230	16	112
Toluene	42	19	13	3	218
m-Xylene	69	10	2	55	6
o-Xylene	105	3	<1	18	1
Napthalene	1	<<1	<1	<1	1
Phenol	3.0	89.0	20.0	0.6	2.5
Furfuryl alcohol	--	--	--	1.6	0.2

Moorman et al, in their foundry studies, have reported on the emissions of polycyclic aromatic hydrocarbons and phenols from no-bake resins as shown in Table 11 (17).

Table 11. Emissions from No-Bake Molds.

Particulate Fraction

Compound	Emission (µg/g particulate) from Binder Systems.	
	Furan	Urethane
Acridine	<0.6	<0.6
Napthalene	<0.6	12
Carbazole	<0.6	<0.6
Phenanthrene	31	230
Benzo(a)anthracene Chrysene	<0.6	5.4
Benzo(a)pyrene	<0.6	<0.6
Dibenzo(a,h)anthracene	<0.6	<0.6

Water Soluble Fraction

Compound	Emission (µg/g sample) from Binder System	
	Furan	Urethane
Phenol	2000	50000
Pentachlorphenol	3	<2
4-Nitrophenol	48	420
2-Nitrophenol	<2	<2
2,4-Dimethylphenol	<2	21

Emory et al in their laboratory studies determined the amount of amines present in the mold effluent using the quasi-stack method (11). The results can be found in Table 12.

Cold Box

The third type of binder is the cold box. The cold box binder systems are relatively new to the foundry industry (5). Their acceptance was facilitated by the increasing prices of oil and natural gas used in the heat activated systems. The cold box process is distinguished from the other processes by the use of a gas or vaporization catalyst to cure the core (22). With the exception of the silicate/CO_2 system, the cold box system is a four step process: blow, gas, purge, strip. The whole process is a relatively fast operation.

There are several different gasses used in the cold box systems. These include amines, sulfur dioxide, and carbon dioxide (8,22). An example of the chemistry of the amine gassed process is a two part resin (1). The first part consists of a phenol formaldehyde Novalak resin and the second part a partially polymerized diisocyanate based on diphenylmethane diisocyanate. The reaction is catalyzed by a tertiary amine, usually either triethylamine, or dimethylethylamine. In the presence of the catalysts, parts I and II form a solid thermoset urethane binder, which binds the sand together (8). If the proper amounts are not added, then the curing will not be complete. Therefore, overgassing has become a general way of practice. Advantages of the cold box system include an increase in productivity and a reduced machinery maintenance cost (5).

Table 12. Amines Present in No-Bake Mold Effluent

Compound	Concentration (mg/m^3) from Binder System				
	Alkyd Isocyanate	Phenolic Urethane	Phenolic No-Bake	Furan No-Bake	Nitrogen Free Furan No-Bake
Aniline	4.5	2.8	<0.2	4.9	<0.2
Triethylamine	<0.2	<0.2	<0.2	<0.2	<0.2
Morpholine	<0.2	<0.2	<0.2	<0.2	<0.2
N,N dimethylformamide	<0.2	<0.2	<0.2	<0.2	<0.2
N,N dimethylaniline	<0.2	<0.2	<0.2	<0.2	<0.2
o-Toluidine	<0.2	<0.2	<0.2	<0.2	<0.2
2,4-Xylidine	<0.2	<0.2	<0.2	<0.2	<0.2
o-Anisidine	<0.2	<0.2	<0.2	<0.2	<0.2
p-Anisidine	<0.2	<0.2	<0.2	<0.2	<0.2
Mesidine	<0.2	<0.2	<0.2	<0.2	<0.2

The binders in the cold box system include phenolic/urethane/amine, phenolic ester, furan/SO_2, epoxy/SO_2, free radical curing (FRC)/SO_2, and silicate/CO_2 (8,22). The phenolic/urethane/amine system is composed of a phenolic formaldehyde Novalak resin reacted with diphenylmethane diisocyanate (1,8). The catalyst of the reaction can be either triethylamine or dimethylamine. The phenolic/ester binder consists of a liquid phenolic resole and a volatile ester (8). The phenolic resole is an alkaline liquid containing: less than 0.5% free formaldehyde, less than 2.0% free phenol, and a significant portion of an inorganic compound. The ester is methyl formate.

The furan/SO_2 system is made up of a furan based resin, an organic peroxide (methyl ethyl ketone peroxide (MEKP)), and sulfur dioxide (5). The MEKP and SO_2 acting together work as the catalyst. The epoxy/SO_2 system contains cumene hydroperoxide, and isopropylbenzene as the first part of the binder (18). The second part consists of bis(2-ethylhexyl)adipate, napthalene, and 1,2,4 trimethyl benzene. The silicate/CO_2 system is composed of sodium silicate and carbon dioxide (8). The FRC (Free Radical

Curing)/SO_2 process consists of a part A and a part B. Part A is an epoxy resin blended with an organic hydroperoxide and solvents and part B is an acrylic or vinyl-ester component with an epoxy resin. Table 13 gives a list of possible HAPs found in the cold box process (2,4,9,20).

Table 13. Possible HAP Emissions from Cold Box Binders.

Phenols	Formaldehyde
Napthalene	Hydrogen Cyanide
Cresol	Isocyanates (MDI)
Aniline	Triethylamine
Benzene	

Laboratory studies by Archibald and Warren (4) showed quantities of chemicals released during the pouring and cooling of the metal castings in molds made by the Ashland process, the FRC process, the SO_2 process, and the phenolic ester process. Hood stack studies similar to those of Scott et al (23) were made on the molds to measure the releases of the thermal decomposition products. All the molds were poured within twenty-four hours of making the mold. The experiment used an irregular gear pattern developed by AFS. The metal used was a class 30 gray iron poured at 2600 °F. The results were reported in mg emission/g binder over a one hour sampling period, except where noted (Table 14).

Table 14. Quantities of Decomposition Products Released for Four Cold Box Binders.

Binder Process	Chemical	Range (mg emission/g binder)
Phenolic Urethane	Formaldehyde	0.01-0.016
	Phenol	1.580-3.890
	Aromatic hydrocarbons	2.220-5.650
	Aromatic isocyanates	0.028-0.069
FRC	Acrylic acid	0.33-0.47
	Hydroxyethyl acrylate	0.25-0.30
	Phenol	2.45-4.35
	Sulfur dioxide	0.08-0.18
Sulfur Dioxide (30 min test)	Sulfur dioxide	9.6
	Aromatic hydrocarbons	2.85
Phenolic Ester	Formaldehyde	0.37-0.57
	Phenol	0.31-0.65
	Aromatic hydrocarbons	0.68-2.78

Green Sand

The most common system used in the production of molds is green sand, which is packed into a mold with no curing. Important properties of the sand are that it must be able to pack tightly, deform slightly without cracking, withstand the pressure of the molten metal, be flowable, and not melt or fuse to the casting at high temperatures (22). Generally green sand is mixed with different additives such as carbons, cereals, starches, celluloses, clays, chemicals, refractories, and water (14). The green sand additives potentially release HAPs to the atmosphere (Table 15). Chemicals released during the pouring and cooling process have been determined by Scott et al. (23) (Table 16).

Table 15. Possible HAP Releases from the Use of Green Sand

Phenols
Toluene
m-Xylene
Napthalene
Acetaldehyde
Hydrogen sulfide
Benzene
Formaldehyde
o-Xylene
Acrolein
Amines (Aniline)

Table 16. Quantities of Chemicals Released in the Green Sand Process.

Chemical	Concentration (mg/m^3)
Sulfur dioxide	12.0
Hydrogen sulfide	39.5
Hydrogen cyanide	5.6
Ammonia	3.1
Nitrous oxides	26.7
Formaldehyde	0.2
Acrolein	0.1
Total Aldehydes	3
Total Aromatic Amines	1
Benzene	29
Toluene	3
m-Xylene	<1
o-Xylene	<1
Napthalene	<1
Phenol	6.2

The amounts of polycyclic aromatic hydrocarbons and phenols released from green sand molds during the cooling process as reported by Moorman et al are given in Table 17 (17).

Table 17. Emissions from Green Sand Molds.

Particulate Fraction

Compound	Emission (µg/g particulate)
Acridine	<0.6
Napthalene	<0.6
Carbazole	<0.6
Phenanthrene	7200
Benzo(a)anthracene \	1100
Chrysene /	
Benzo(a)pyrene	230
Dibenzo(a,h)anthracene	<0.6

Water Soluble Fraction

Compound	Emission (µg/g sample)
Phenol	1000
Pentachlorphenol	<2
4-Nitrophenol	<2
2-Nitrophenol	<2
2,4-Dimethylphenol	<2

A more detailed list of HAP emissions can be found in the next section of this report.

Along with the HAP emissions from these processes are other emissions. Table 18 lists some other typical emissions found when pouring metal into molds made with binders from these processes (1,2,4,8,9,11,13,20,21,23).

Table 18. Non HAP Emissions from Binders.

Heat Activated	Ethyl Alcohol
	Carbon Monoxide
	Carbon Dioxide
	Furfuryl Alcohol
	Ammonia
	Sulfur Dioxide
	Nitrous Oxides
No-Bake	Sulfur Dioxide
	Furans
	Acetone
	Nitrous Oxides
Cold Box	Carbon Monoxide
	Sulfur Dioxide
	Methyl Formate

FIELD INFORMATION ON POTENTIAL AIR EMISSIONS OF HAP'S FROM IRON AND STEEL FOUNDRY BINDERS AND OTHER CHEMICALS

Potential air emissions of HAP's from binders and other chemicals used in iron and steel foundries were assessed using information obtained from the technical literature, suppliers, MSDS's, foundry contacts, and from AFS educational workshops. Information from the literature was presented in the previous section.

SUPPLIER CONTACTS

Suppliers of chemicals to foundries were contacted by form letter (see Appendix) and asked to submit information on binder chemical emissions. Phone calls to four major different binder manufacturers also yielded applicable information. Material Safety Data Sheets (MSDS) were obtained from these manufacturers. One supplier provided information by binder type and process. Another supplier provided information with only binder type detail. Two other suppliers have indicated that they will send information, but none has been received to date. Several iron foundries were also contacted for information but only a few responded with information.

WORKSHOPS

One of the investigators attended an AFS workshop on coremaking at the AFS training center in Chicago in April, 1992. The workshop provided valuable information from the instructors and attendees.

FOUNDRY VISITS

Visits have been made to six major foundries in Alabama to discuss current process information and extent of data available on air emissions of hazardous air pollutants from coremaking, pouring, and shakeout operations. These visits have proven very useful to this project, especially in identifying possible sample locations and potential sampling methods.

OTHER ACTIVITIES

As mentioned earlier, this project was proposed originally as an information collection and analysis effort to aid AFS members in complying with environmental regulations. The focus of the program was shifted to concentrate on immediate industry concerns.

USEPA COORDINATION

Several trips have been made to Durham, NC to coordinate activities with USEPA's Office of Air Quality Planning and Standards. James H. Maysilles, the EPA Project Officer, is our designated contact for the project. The EPA contractor for developing the Background Information Document is Research Triangle Institute (Durham, NC).

QUESTIONNAIRE DEVELOPMENT

A questionnaire was developed to help foundries begin assessing air emission potentials for the different processes. Worksheets were prepared for scrap pretreatment, melt furnace, core room, molding, pouring, shakeout, and sand reclaiming. The questionnaire was tested on several foundries in Alabama, but contact with USEPA's Office of Air Quality Planning and Standards indicated that their screening information request (the "short form"), and maximum achievable control technology (MACT) standards development information request (the "long form"), were to be issued shortly. To prevent confusion between the documents, we suspended work on our version and concentrated on coordinating our efforts with the USEPA in developing the questionnaire and in helping the foundryman understand and complete the required forms, which are now scheduled to be mailed in October and November. Our notes to support the completion of the forms, the forms themselves, and our original questionnaire draft are included in the Appendix of this report.

DISCUSSION OF RESULTS

The emissions of HAP's from iron and steel foundries can generally be classified as metals or organics.

METALS

Emissions from melting furnaces are primarily volatile metals, which are generally controlled by particulate emission control devices. These emissions depend upon the type of scrap melted and on the type of melting furnace. Any polymers, especially vinyl polymers, in the scrap may generate organic emissions, but the levels of organic emissions to be expected have not been quantified. Afterburners to control CO emissions in cupolas may also give sufficient control of any organic compound emissions. A study of emissions from melting operations was beyond the scope of the present study. Metal emissions from core and mold making, and shakeout are considered to be insignificant. Metal emissions from pouring depends on the alloy poured and the pouring temperature and are not included in this study.

ORGANIC COMPOUND EMISSIONS

The potential emissions of HAP's from production of cores and molds are generally volatile organic compounds that result from unreacted components of the resin, solvents, or catalysts. Potential HAP emissions from pouring and shakeout are pyrolysis and oxidation products from the binder resins. The compounds that potentially could be emitted in these operations are shown in Table 19, which contains the 189 HAP's included in the CAAA. Entries in the table have been coded with EPA's suggested code on their proposed foundry industry questionnaire:

A = specific HAP is known to be emitted
B = specific HAP is known NOT to be emitted
C = not reason or data to assume the HAP is emitted
D = specific HAP has been reported in the literature in trace amounts

Excluding metals, only 16 of the 189 HAP's have been identified in this study as being potentially emitted in foundry operations. These HAP's have been identified by type, but quantitative data on levels of emissions are very scarce and generally not available. This will be discussed in more detail later.

Table 20 lists the binder systems reviewed in this study, along with the chemical ingredients, approximate use level, and known HAP emissions from core making, pouring, and shakeout. Binder systems not included in this study were oil/urethane or alkyd/urethane binders, which are declining in popularity and are known to contain the HAP's cobalt and lead.

TABLE 19
POTENTIAL EMISSIONS OF HAP'S FROM FOUNDRIES

CAS Number	Chemical	Code
75070	acetaldehyde	B
60355	acetamide	C
73058	acetonitrile	C
98862	acetophenone	C
53963	2-acetylaminofluorene	C
107028	acrolein	B
79061	acrylamide	C
79107	acrylic acid	C
107131	acrylonitrile	C
107051	allyl chloride	C
92671	4-aminobiphenyl	C
62533	aniline	B
90040	o-anisidine	C
1332214	asbestos	C
71432	benzene (including gasoline)	A
92875	benzidine	C
98077	benzotrichloride	C
100447	benzyl chloride	C
92524	biphenyl	C
117817	bis(2-ethylhexyl)	C
	phthalate (DEHP)	C
542881	bis(chloromethyl)ether	C
73252	bromoform	C
106990	1,3-butadiene	C
156627	calcium cyanamide	C
105602	caprolactam	C
133062	captan	C
63252	carbaryl	C
75150	carbon disulfide	C
56235	carbon tetrachloride	C
463581	carbonyl sulfide	C
120809	catechol	C
133904	chloramben	C
57749	chlordane	C
7782505	chlorine	C
79118	chloroacetic acid	C
532274	2-chloroacetophenone	C
108907	chlorobenzene	C
510156	chlorobenzilate	C
67663	chloroform	C
107302	chloromethyl methyl ether	C
126998	chloroprene	C
1319773	cresols/cresylic acid	A
95487	o-cresol	C
108394	m-cresol	C
106445	p-cresol	C
98828	cumene	C
94757	2,4-D salts and esters	C
3547044	DDE	C
334883	diazomethane	C
132649	dibenzofuran	C
96128	1,2-dibromo-3-chloropropane	C
84742	dibutylphthalate	C
106467	1,4-dichlorobenzene(p)	C
91941	3,3'-dichlorobenzidene	C
111444	dichloroethyl ether	C
542736	1,3-dichloropropene	C
62737	dichlorvos (dichlorovos)	C
111422	diethanolamine	C
121697	N,N-dimethylaniline	C
91667	N,N-diethylaniline	C
64673	diethyl sulfate	C
119904	3,3'-dimethoxybenzidine	C
60117	dimethylaminoazobenzene	C
119937	3,3'-dimethylbenzidine	C
79447	dimethylcarbamoyl chloride	C
68122	dimethylformamide	C
57147	1,1-dimethyl hydrazine	C
131113	dimethyl phthalate	C
77781	dimethyl sulfate	C
534521	4,6-dinitro-o-cresol and salts	C
51285	2,4-dinitrophenol	C
121142	2,4-dinitrotoluene	C
123911	1,4-dioxane (1.4-diethyleneoxide)	C
122667	1,2-diphenylhydrazine	C
106898	epichlorohydrin	C
106887	1,2-epoxybutane	C
140885	ethyl acrylate	C
100414	ethylbenzene	C
51796	ethyl carbamate (urethane)	C
75003	ethyl chloride (chloroethane)	C
106934	ethylene dibromide	C
107062	ethylene dichloride	C
107211	ethylene glycol	C
151564	ethyleneimine (aziridine)	C
75218	ethylene oxide	C
96457	ethylene thiourea	C
75343	ethylidene chloride	C
50000	formaldehyde	A
76448	heptachlor	C
118741	hexachlorobenzene	C
87683	hexachlorobutadiene	C
77474	hexachlorocyclopentadiene	C
67721	hexachloroethane	C
822060	hexamethylene diisocyanate	C
680319	hexamethylphosphoramide	C
110543	hexane	C
302012	hydrazine	C
7647010	hydrochloric acid	C
7664393	hydrogen fluoride	C
7783064	hydrogen sulfide	C
123319	hydroquinone	C
78591	isophorone	B
58899	lindane (all isomers)	C
108316	maleic anhydride	C
675361	methanol	A
72435	methoxychlor	C
74839	methyl bromide (bromomethane)	C
74873	methyl chloride (chloromethane)	C
71556	methyl chloroform	C
78933	methyl ethyl ketone (2-butanone)	C
60344	methyl hydrazine	C
74884	methyl iodide (iodomethane)	C
108101	methyl isobutyl ketone (hexone)	C
624839	methyl isocyanate	C
80626	methyl methacrylate	C
1634044	methyl-tert-butyl ether	C
101144	4,4-methylene bis	C
75092	methylene chloride	C
101688	MDI	A
101779	4,4-methylenedianiline	C
91203	naphthalene	A
98953	nitrobenzene	C
92933	o-nitrobiphenyl	C
100027	4-nitrophenol	C
79469	2-nitropropane	C
684935	n-nitroso-n-methylurea	C
67759	n-nitrosodimethylamine	C
59892	n-nitrosomorpholine	C
56382	parathion	C
82688	pentachloronitrobenzene	C
87865	pentachlorophenol	C
108952	phenol	A
106503	p-phenylenediamine	C
75445	phosgene	C
7803512	phosphine	C
7723140	phosphorus	C
85449	phthalic anhydride	C
1336363	polychlorinated biphenyls	C
1120714	1,3-propane sultone	C
57578	beta-propiolactone	C
123386	propionaldehyde	C
114261	propoxur (Baygon)	C
78875	propylene dichloride	C
75569	propylene oxide	C
75558	propylene imine	C
91225	quinoline	C
106514	quinone	C
100425	styrene	C
96093	styrene oxide	C
1746016	2,3,7,8-tetrachloro-dibenzo-p-dioxin	C
79345	1,1,2,2-tetrachlorethane	C
127184	tetrachloroethylene	C
7550450	titanium tetrachloride	C
108883	toluene	A
95807	2,4-toluene diamine	C
584849	2,4-toluene diisocyanate	C
95534	o-toluidine	C
8001352	toxaphene (chlorinatedcamphene)	C
120821	1,2,4-trichlorobenzene	C
79005	1,1,2-trichloroethane	C
79016	trichloroethylene	C
95954	2,4,5-trichlorophenol	C
88062	2,4,6-trichlorophenol	C
121448	triethylamine	A
1582098	trifluralin	C
540841	2,2,4-trimethylpentane	C
108054	vinyl acetate	C
593602	vinyl bromide	C
75014	vinyl chloride	C
75354	vinylidene chloride	C
1330207	xylenes	A
95476	o-xylenes	C
108383	m-xylenes	C
106423	p-xylenes	C
0	antimony compounds	C
0	arsenic compounds	C
0	beryllium compounds	C
0	cadmium compounds	C
0	chromium compounds	C
0	cobalt compounds	C
0	coke oven emissions	C
0	cyanide compounds	A
0	glycol ethers	C
0	lead compounds	C
0	manganese compounds	C
0	mercury compounds	C
0	fine mineral fibers	C
0	nickel compounds	C
0	polycyclic organic matter	A
0	radionuclides (including radon)	C
0	selenium compounds	C

TABLE 20
WASTE MANAGEMENT STUDIES OF FOUNDRIES
MAJOR WASTE STREAMS PROCESS: COREMAKING

				POTENTIAL HAP[1] PRODUCTS		
Binder System	**Type**	**Major Reactant Chemicals**	**Use Level (sand basis)**	**COREMAKING**	**POURING**	**SHAKEOUT**
Cold Box	Phenolic Urethane	phenolics isocyanates triethylamine	0.4-1.2% 0.4-1.2% 0.1%	formaldehyde MDI phenol triethylamine	benzene cresole/cresylic acid formaldehyde MDI napthalene phenol toluene polycyclic-organic matter cyanide compounds	benzene cresole/cresylic acid formaldehyde MDI napthalene phenol toluene polycyclic-organic matter cyanide compounds
	Phenolic Ester	phenolic resins methyl formate	1-2% 0.75-1.5%	formaldehyde phenol	benzene cresole/cresylic acid formaldehyde napthalene phenol toluene polycylic-organic matter	benzene cresole/cresylic acid formaldehyde napthalene phenol toluene polycyclic-organic matter
	Silicate-CO_2	sodium silicate CO_2	1.5-4.0%			

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				POTENTIAL HAP[1] PRODUCTS		
Binder System	Type	Major Reactant Chemicals	Use Level (sand basis)	COREMAKING	POURING	SHAKEOUT
Heat Activated	Shell (Resin Coated sand)	phenolic resin hexamethyltetramine	4-5%	formaldehyde methanol phenol	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter
	Phenolic Hot Box	phenolic resin acid chloride salt	1.5-2.0%	formaldehyde phenol	benzene cresole/cresylic acid formaldehyde napthalene phenol toluene polycyclic-organic matter cyanide compounds	benzene cresole/cresylic acid formaldehyde napthalene phenol toluene polycyclic-organic matter cyanide compounds
No Bake	Furan/ Acid	furfuryl alcohol benzenesulfonic acid	0.9-2.0% 0.3-0.9%	benzene methanol phenol toluene	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter cyanide compounds	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter cyanide compounds

Binder System	Type	Major Reactant Chemicals	Use Level (sand basis)	POTENTIAL HAP[1] PRODUCTS		
				COREMAKING	POURING	SHAKEOUT
<u>No Bake (Cont'd)</u>	Phenolic/ acid	phenolic resin sulfonic-type acid catalyst	1.5-2.0% 0.3-0.9%	formaldehyde methanol phenol toluene	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter
	Phenolic/ Ester	phenolic resins esters	1.5-2.0% 0.3-0.5%	formaldehyde phenol	benzene cresole/cresylic acid formaldehyde napthalene phenol toluene polycyclic-organic matter	benzene cresole/cresylic acid formaldehyde napthalene phenol toluene polycyclic-organic matter
	Phenolic Urethane	phenolic resin isocyanates amine catalyst	1-2% " 0.1%	formaldehyde MDI phenol	benzene cresole/cresylic acid formaldehyde napthalene phenol toluene polycyclic-organic matter cyanide compounds	benzene cresole/cresylic acid formaldehyde napthalene phenol toluene polycyclic-organic matter cyanide compounds

[1] HAP = hazardous air pollutant

The previous lists of HAP's are inclusive of emissions which may occur in several different locations in a foundry. It probably will be necessary to pinpoint more accurately which HAP's are emitted from each area of the plant. Therefore, some discussion will be made of the potential emissions from several areas of the plant.

CORE AND MOLD MAKING

Actual published quantitative emission data taken in core rooms were not found. Emissions of HAP's in core and mold making up to now have been of concern mainly for occupational health and safety. The main reason for needing to know the level of emissions has been to determine ventillation requirements. Mosher (20) recently has compiled data from suppliers and manufacturers of binder chemicals to determine the fate of the ingredients put into the coremaking process. This document was prepared to assist foundries in filling out the EPA form R on emissions. The fate of the chemical ingredients was categorized as percent that was reacted and no longer existed after coremaking, percent not changed in the process and remained in the core, and percent evaporated to give an airborne emission. Therefore, these data can be used to give estimates of emissions from core and mold preparation areas. For example, Tables 21 through 23 show sample calculations for naphthalene, formaldehyde, and methanol evaporation emissions from three of the common binder systems that would be expected in the core room.

Table 21. Estimated Naphthalene Emissions from Phenolic Urethane Cold Box Binder

Sample Calculation 1

Binder System: Phenolic Urethane Cold Box

Source of Data: UA/AFS Mosher

Chemical: Naphthalene

Assumptions:
Concentration in Binder: 6.04%
Use Level: 0.8%
Evaporation Rate: 50%
No Air Capture or Control Devices

Pounds of Binder Needed to Generate 10 Tons/Year Emissions in Coremaking Operations:

$20,000/(0.0604*0.5) = 662,252$ pounds of binder

Pounds of Core Sand Needed at Above Binder Use Rate to Generate 10 Tons/Year Emissions in Coremaking Operations: $662,252/0.008 = 82,781,500$ pounds of core sand

Table 22. Estimated Formaldehyde Emissions from Furan No Bake Binder

Sample Calculation 2

Binder System: Furan No Bake

Source of Data: UA/AFS Mosher

Chemical: Formaldehyde

Assumptions:

Concentration in Binder: 1.70%
Use Level (Core Sand Basis): 1.5%
Evaporation Rate: 10%
No Air Capture or Control Devices

Pounds of Binder Needed to Generate 10 Tons/Year Emissions in Coremaking Operations:

20,000/(0.017*0.1) = 11,764,706 pounds of binder

Pounds of Core Sand Needed at Above Binder Use Rate to Generate 10 Tons/Year Emissions in Coremaking Operations:

11,764,706/0.015 = 784,313,733 pounds of core sand

Table 23. Estimated Methanol Emissions from Phenolic No Bake - Acid Binder

Sample Calculation 3

Binder System: Phenolic No Bake - Acid

Source of Data: UA/AFS Mosher

Chemical: Methanol

Assumptions:

Concentration in Binder: 4.00%
Use Level: 0.6%
Evaporation Rate: 50%
No Air Capture or Control Devices

Pounds of Binder Needed to Generate 10 Tons/Year Emissions in Coremaking Operations:

20,000/(0.04*0.5) = 1,000,000 pounds of binder

Pounds of Core Sand Needed at Above Binder Use Rate to Generate 10 Tons/Year Emissions in Coremaking Operations:

1,000,000/0.006 = 166,666,667 pounds of core sand

POURING AND SHAKEOUT

Laboratory data on emissions from pouring and cooling for one hour for most common binder systems have been reported. Although the studies were made for workplace health and safety considerations, quantities of the major organic compounds emitted can be calculated from the data. The experiments were made to give a comparison among binder systems, and no parameter studies were made (Scott et al. (23). The casting was an irregular gear, which weighed approximately 40 kg with the gating system and riser. The sand weighed approximately 100 kg to give a sand-to-metal ratio of 2.5. The pouring temperature was 1450 °C. Emissions data were reported in concentrations (ppm), but with the specified gas flow rate of 1000 L/min through the stack the mass of emissions of each component can be calculated. They made measurements on 10 hot-box and no-bake binders, as well as for green sand and dry sand. Emory et al (11) used an identical setup to study nitrogen compound emissions from three hot-box and three no-bake binder systems. A third set of experiments, again using the same setup, was made by Archibald and Warren (4) on four cold-box binder systems. Calculations were made from Scott et al (23) to put their results into the same format as results from Archibald and Warren (4) (Table 24).

Table 24. Comparison of Emission Data Between Scott et al (23) and Archibald and Warren (4)

	Formaldehyde mg/g resin	Phenol mg/g resin	Aromatics mg/g resin
Alkyd isocyanate (23)	0.11	0.36	44
Phenolic urethane (23)	0.025	14	21
Ashland no-bake (4)	0.051	11.7	17.2

These data appear to be quite consistent and can be used to get an order-of-magnitude estimate of emissions of various HAP's during the pouring and cooling part of the casting process.

CONCLUSIONS

The data in the literature on organic HAP emissions are of two types: (1) identification of chemical types and their concentrations in the workplace needed for worker health and safety, and (2) emissions during pouring and cooling. There are no emission data for shakeout. The pouring and cooling emissions were made for a single type of casting using the same metal-to-sand ratio and grey iron. Data were reported either as concentrations in the gas or an milligrams of HAP per gram of binder resin. While these articles give some idea of the order of magnitude of emissions, they do not give the effect of parameters on the emission level. It is not clear that reporting the data as mg HAP/g resin is the proper parameter if the sand-to-metal ratio changes. There are no data at different metal temperatures, so that emission factors based on this literature cannot be used for steel casting. Since shakeout may occur at a different part of the plant, and because pyrolysis products may be trapped in the sand before shakeout, the effect of cooling time on shakeout emissions is needed. It is apparent that additional research is needed to determine the important parameters that control HAP emissions.

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OUTLINE OF MANUAL FOR CONTROL OF EMISSIONS FROM FOUNDRY OPERATIONS

I. Introduction
II. General Purpose and Use of Manual
III. Processes. This section will contain the process description for the 18 processes that EPA has identified for foundry operations. Each subsection will contain:
    A. Process Title (for example Scrap Preheating)
        1. Process Description
        2. Emission Points
        3. Emissions
        4. Control Technology/Strategy
    B. Repeated for the other 17 processes (Furnace Operations, Ladle Metallurgy Operations, Sand and Binder Preparation, Pattern Release Coating, Sand Compaction and Distribution, Gas Curing, Core and Mold Drying and Curing, Coating Preparation, Core and Mold Coating, Coating and Drying, Pouring, Cooling Process, Casting Punchout and Shakeout, Mechanical Finishing, Heat Treatment, Chemical Finishing, and Sand Reclamation)
IV. General Control Technologies
    A. Air Emissions
    B. Water Pollution
    C. Solid Waste