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DOCUMENT NO. HW-SA-3015

COPY NO. 1

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TITLE

HEALTH AND SAFETY GUIDES FOR CHEMICAL HANDLING: THE RARE EARTH METALS AS AN EXAMPLE

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AW-SA-3015

HEALTH AND SAFETY GUIDES FOR CHEMICAL HANDLING:

THE RARE EARTH METALS AS AN EXAMPLE.

Prepared for Presentation Before the Northwest
Association of Occupational Medicine
May 11, 1963
at Richland, Washington

by R. H. Scott

Summary

Information about health and safety considerations in handling the rare earth metals is used to exemplify the application of Chemical Safety Guides in a research-oriented industrial environment.

The professional interests of this audience all focus on protecting the health and safety of workers. Toward this end many types of safeguards are employed and many become standardized techniques. However, in an environment where technologies are being supplanted continually by new technologies, the race to provide parallel safeguards becomes a hot pursuit. A most useful technique under these conditions is to enlist the help of those we wish to protect. A helpful tool for accomplishing this end is to furnish them with specific knowledge of the hazards they must contend with.

Knowledge is not prescribed here as a substitute for the useful physical techniques in providing health and safety. But, before these techniques can be applied sensibly, knowledge about hazards is a prerequisite. An example of the overt effort in Hanford Laboratories to put useful information about toxicity,

Work Performed Under Contract No. AT(45-1)-1350
Between the Atomic Energy Commission
And General Electric Company

fire and explosion hazards, or other dangers into the hands of the personnel exposed is the purpose of this paper.

This need for information seems particularly acute among users of chemicals. Why and to what extent a chemical is hazardous is indispensable in an environment where process change is a constant concern; where uses for new or unfamiliar chemicals and new applications of familiar chemicals are being devised continually. Therefore, to help the chemical researchers and the chemical processors protect themselves against hazards of the materials they deal with, a need was felt to bring pertinent information into usable, available form. The form adopted in Hanford Laboratories was a series of "Chemical Safety Guides" for inclusion as a special section in our Manual of Health and Safety.

A chemical safety guide is not a new concept. Many business, industrial, and professional organizations produce them, and other sources are available to the diligent searcher. Some of those sources are devoted to a single class of hazards, fire for example; others omit desirable information. The motive here was to incorporate into one package an adequate body of safety and hygiene information to furnish ready guidance in the safe pursuit of work with chemicals. Typical sources that contributed to the guides that we evolved are shown in Slide 1. From this variety of materials we undertook to condense appropriate chemical hazard information into the format shown in Slide 2.

The original selection of chemicals for inclusion in the series of Chemical Safety Guides was made from a laboratory-by-laboratory inventory. Attention was focused first on the ones used in bulk both in Hanford Laboratories and in the manufacturing components at Hanford Atomic Products Operation. For those not in quantity use, the criterion used was their prominence as recognized, hazardous substances. In the first fifteen months, a total of 64 Chemical Safety Guides was prepared on this basis. Eleven more have just been added.

An addition to the guides is made for any of three reasons.

1. If a process change introduces a previously unused chemical and that chemical has a potential hazard, a new guide is written.
2. If a new hazard is disclosed for a familiar chemical, a new or revised guide is prepared.
3. If a process or an experiment introduces a relatively unfamiliar chemical, a search is made for information related to its hazards and the information is brought together as a new chemical safety guide.

This last category was the motive for the recent addition of Chemical Safety Guide No. 67, devoted to "Yttrium and the Rare Earth Metals." This guide was chosen for this paper to exemplify part of our program to guard the health and safety of laboratory and plant workers by providing them with knowledge as a protective tool.

In the scheme of chemical elements, there are fifteen Rare Earths. Fourteen of them have stable, non-radioactive forms. Shortly after these 14 and yttrium came under investigation in our research programs, inquiries from the researchers and from machinists about possible hazards motivated the preparation of this new Chemical Safety Guide.

The opportunity to lump under one Guide the fifteen elements listed in Slide 3 arises from a remarkable coincidence in their chemical properties. As noted in Slide 3, the atomic numbers starting with lanthanum run consecutively from 57 through 71. The ordinary expectation with an increase of one in the atomic number is a coinciding addition of an electron in one of the outer shells of the atom. Since the electron configurations in the outermost shells determine the chemical behaviors of elements, consecutive elements in the atomic table normally possess significantly different chemical properties. In the series starting with lanthanum, however, there are six shells of electrons, but the electron additions occur in the fourth shell, while the fifth and sixth shells remain virtually the same throughout the series. Yttrium, with atomic number 39, differs only in having one less inner shell. Thus the unchanging outer shells, which are little affected by the distant electron additions, show forth in very similar chemical behaviors among these fifteen elements.

The common chemical behaviors of yttrium and the rare earth metals are also evinced in what is known about this family of elements from the health and safety standpoints. Using the outline format given in Slide 2 as a road map, the information derived for this particular Chemical Safety Guide can be reviewed briefly. For convenience, however, let's start at the bottom with Reaction Hazards and work toward a destination at the top of the map.

According to a listing of hazardous reactions in a forthcoming publication by National Fire Protection Association, these metals will decompose carbon tetrachloride. They also share the property of burning vigorously in chlorine, bromine, and fluorine gases. This information can be helpful to chemists as a warning against chance or purposeful mixture of the rare earths with carbon tetrachloride or the halogen gases. Possibly it is helpful to metallurgists, too, to know that this family of metals forms hydrides which ignite in moist air.

Nearby, at the locale of Fire Hazards, there is other evidence of dangerous chemical behavior. Yttrium and the rare earths are pyrophoric, that is, in the presence of moist air, they tend to burn. This property is particularly prominent in praseodymium, neodymium, lanthanum, europium, and cerium. The precaution learned here is that these metals should be machined without water as a cooling agent and that waste turnings and small particles should be disposed of promptly to prevent fires.

Under the heading of Eye Hazards, there is concern over yet another chemical property common to all these elements: they all have the ability to form complexes with organic substances. This property relates importantly to findings in experiments on the eyes of rabbits. When rare earth metals penetrate into the cornea they have an affinity for the connective tissue, where they rapidly form insoluble complexes. These complexes, being quite immobile, result quickly in a permanent opacity in the eye. The ability of rare earths to affect the eye in this fashion is 40 to 80 times that of alkaline earth metals like calcium and barium. The industrial safety inference of these findings is that under conditions where metal fragments from machining or metal forming might penetrate the cornea, severe damage could result unless immediate removal of the particle is accomplished. Better still, of course, is to provide protection so that the eye cannot experience this kind of insult.

Ingestion Hazards are considered extremely unlikely in industry. Carrying on to the last main heading, Inhalation Hazards, the degree of jeopardy is arrived at by inference from animal experiments, using injections of various salts of the rare earth metals in solution. Favorable industrial experience with a very few of these rare earth elements also helped in formulating temporary safety measures.

From the animal experiments, it was observed that the most frequent effects were lesions of the liver and kidney, with acute passive congestion of the lungs also appearing. The lighter rare earths deposited mainly in the liver; the heavier metals tended more to bone storage. However, in the final analysis, the lesions that were produced were quite similar for every one of the metals tested.

Also typical of the findings that confirmed the similar toxic natures of these elements were the experimental results on lethal doses. One set of these is shown in Slide 4. This figure compares doses that were lethal within a one-week period to 50% of the guinea pigs in a tested population. Notice that the element with the lowest LD_{50} and therefore the most toxic to these animals, was yttrium. Still, yttrium was less than twice as lethal as the least toxic metal, lutecium.

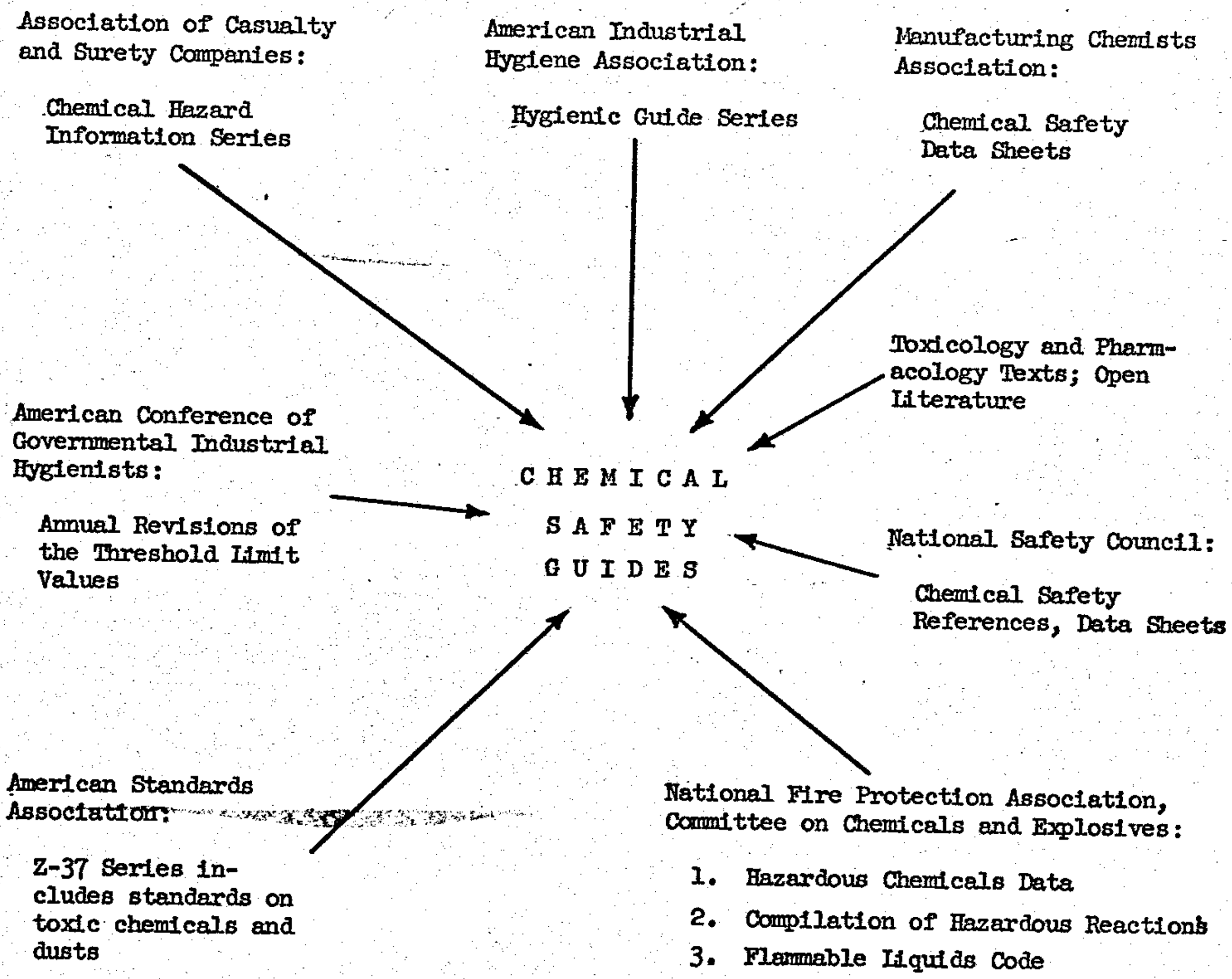
In about 1956, with only this sort of toxicity data available, there arose a need to adopt a threshold limit value for human inhalation of yttrium. As a safeguard in burgeoning research with yttrium, the value selected was 5 milligrams per cubic meter of air. Adherence to this limit has yielded a satisfactory experience of no human intoxication by yttrium. Similar favorable results were experienced with cerium and lanthanum, the two most used rare earths.

With this background of experience and the previously mentioned evidence that yttrium is the most toxic of these fifteen metals, the adoption of 5 milligrams per cubic meter as a threshold limit value for <u>all</u> the rare earths seemed a reasonable risk as a guiding number in this Chemical Safety Guide.

The final destination on this reverse guided tour through a Chemical Safety Guide is the Emergency Procedure locale. The evaluation arrived at in preparing this guide was that no advice from an emergency perspective was needed since the metals could not be classified highly toxic. With reasonable care in handling the small quantities of rare earth metal involved in our current work, hazardous exposures would not be expected unless a fairly large piece of rare earth metal were to burn entirely to the oxide. The prescribed machining precautions make a fire unlikely. Also, since all machining work requires eye protection the eye hazard appears remote. If future plans should foresee bulk use of any of these fifteen elements a re-evaluation of the Chemical Safety Guide would be in order.

With the ready availability of this scope of information about chemical hazards, it is felt that researchers and processors will be able to plan their work with greater confidence in safety.

SLIDE 1


Association of Casualty and Surety Companies:
Chemical Hazard Information Series
American Industrial Hygiene Association:
Hygienic Guide Series
Manufacturing Chemists Association:
Chemical Safety Data Sheets
Toxicology and Pharmacology Texts; Open Literature
American Conference of Governmental Industrial Hygienists:
Annual Revisions of the Threshold Limit Values
CHEMICAL SAFETY GUIDES
National Safety Council:
Chemical Safety References, Data Sheets
American Standards Association:
Z-37 Series includes standards on toxic chemicals and dusts
National Fire Protection Association, Committee on Chemicals and Explosives:
1. Hazardous Chemicals Data
2. Compilation of Hazardous Reactions
3. Flammable Liquids Code

S L I D E 2

CHEMICAL SAFETY GUIDE NO. __

CHEMICAL NAME

Emergency Procedures

INHALATION -

INGESTION -

EYES & SKIN -

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Formula:
Molecular Wt.:
Boiling Point:
Melting Point:

Threshold Limit Value:
Flash Point:
Explosive Limits:
Synonyms:

==

Inhalation Hazard

Ingestion Hazard

Skin and Eye Hazard

Fire and Explosion Hazard

Reaction Hazards

S L I D E 3

		Electron Totals in Inner Layers	Electron Distribution in Outer Three Layers		
57	Lanthanum	28	18	8 + 1	2
58	Cerium	28	18 + 2	8	2
59	Praseodymium	28	18 + 3	8	2
60	Neodymium	28	18 + 4	8	2
62	Samarium	28	18 + 6	8	2
63	Europium	28	18 + 7	8	2
64	Gadolinium	28	18 + 7	8 + 1	2
65	Terbium	28	18 + 8	8 + 1	2
66	Dysprosium	28	18 + 10	8	2
67	Holmium	28	18 + 11	8	2
68	Erbium	28	18 + 12	8	2
69	Thulium	28	18 + 13	8	2
70	Ytterbium	28	18 + 14	8	2
71	Lutecium	28	18 + 14	8	2
39	Yttrium	10	18	8 + 1	2

S L I D E 4

TOXICITIES OF RARE EARTH CITRATES TO GUINEA PIGS
LD_{50} AT 168 HOURS