

1

3,238,148

**SHIELDING CONCRETE AND AGGREGATES**  
Philip S. Osborne, San Pedro, Calif., assignor to Osborne  
Associates, Los Angeles, Calif., a partnership  
No Drawing. Filed Apr. 2, 1962, Ser. No. 184,568  
7 Claims. (Cl. 252-478)

In general, the present invention relates to an inexpensive, strong, durable filler material for shielding against neutrons and gamma radiation over a wide energy spectrum. More specifically, the present invention relates to an aggregate, the concrete produced from said aggregate and methods for producing said aggregate and concrete for shielding against the radiations containing neutron and gamma ray components.

It has long been known that radioactive emanations do substantial biological damage. In addition, normal structural materials will often suffer deleterious effects when exposed to the various types of radiation. Since in recent years there have been greatly increased utilization of radiation and radioactive material the problem of protection against such radiation effects has become increasingly important. Particularly with the advent of the cyclotron, the nuclear reactor and other devices and processes wherein radiation in enormous quantity and of great energy may be produced, the problem of shielding against such radiation is quite complicated.

One problem is that during the operation of a neutronic reactor, various types of radiation are admitted with various energy ranges, depending upon the composition and configuration of the reactor and upon its previous operation history. The most important species of such radiations are the gamma rays and neutrons. Not only do each of these species of radiation react with matter in a substantially different manner, but radiation of a single species may react differently with the same matter depending upon the energy level of the radiation. Consequently, an efficient reactor shielding material must be capable of performing the complex function of satisfactorily attenuating simultaneously each of the species in the reactors composite radiation spectrum.

Another problem is that the efficiency of a material for shielding purposes is determined primarily by its efficiency per unit thickness in radiation attenuation. The weight and volume of a shield enveloping a radioactive system increase approximately as the cube of the shielding thickness, with a consequent similar increase of other dependent factors such as size of supporting structures and foundation, total cost and the like. Thus, it is particularly important to employ shielding of superior efficiency per unit thickness. However, it is also important that the weight, volume and cost of the shielding material be at a minimum. For example, when neutronic reactors are employed for the generation of motive power in ships, the magnitude of the weight and bulk of the shielding will often be the critical factor in determining the practicability of the power unit.

In addition to the problems of attenuating many species of radiation over a wide energy spectrum and achieving such attenuation efficiently, another problem is that the shielding material should be plastic, i.e. be capable of being formed into any desired shape and fitted to irregular shapes. As will be readily understood, most reactors involve curved surfaces such as spheres, s-shaped bends etc., so that sheets and slabs of shielding material would not be suitable.

In the past, because of its low cost, ordinary concrete has been a commonly used inorganic plastic material for reactor shielding. However, with the present increasing magnitudes of reactor size and radiation flux, it has been found that ordinary concrete would result in exces-

2

sively thick shields to be used in most installations. Consequently, much effort and time has been devoted to the improvement of the attenuation efficiency of concrete while maintaining its high strength. The present state of the art in this respect is illustrated by Patent No. 2,726,339, granted to Lyle B. Borst, and issued to the United States Atomic Energy Commission. In the Borst patent the attenuation efficiency of ordinary concrete is improved by incorporating materials such as lead or iron in its free elemental stage and dispersing such iron or lead as punchings, balls or pellets throughout the concrete. By incorporating such materials in their free elemental state, Borst is able to increase the density of the resulting product above regular concrete and thereby obtain increased attenuation efficiency. In addition, Borst disclosed the use of boron in its free elemental state as an additive to the concrete composition to absorb thermal neutrons and reduce the flux of gamma rays. However, as disclosed by Borst himself, his improvement of the shielding properties of concrete has several limitations. First, Borst primarily relied upon the use of metals such as lead in their free elemental state. Second, Borst was limited by the need to use masses of greater than about shot-size since masses smaller than such shot-size generally detracted from the structural and the chemical properties of the shielding. Most important, the data set forth by Borst shows that the increased attenuation efficiency is due solely to the increase of density of the resulting concrete.

It should also be noted that Borst disclosed that elements such as lead and boron could also be used in minor proportion in mineral form, specifically litharge and colemanite, respectively. However, it has been found in practice that the use of such minerals in ordinary concrete has a very substantial deleterious effect on the structural strength of the concrete. For example, the solubility of the minerals in the alkaline environment of concrete seems to release salts or gels at the surface of the aggregate particles and thus greatly weakens the bond between the matrix and the aggregate. In any event, it is the common experience that if only 0.1 percent of litharge is added to a Portland cement concrete, the Portland cement will not even set. Similarly, when colemanite is added to the concrete even in very low percentages, it has been found that frequently the concrete will not set. For example, at one Atomic Energy Commission installation in Idaho, where colemanite was incorporated in the concrete to be used in the shielding, the shielding concrete did not set and an expensive replacement operation was necessitated.

In general, the present invention relates to a composition which is an inexpensive, strong filler for inorganic or organic plastic material and which is adapted to shield against neutrons and gamma radiation over a wide energy spectrum. The present invention involves generally not only such composition but also methods of producing such composition. More particularly, the present invention involves a method of producing a greatly improved concrete which not only has unexpectedly high attenuation efficiency but also has very high strength. Also, the present invention involves a method of producing an aggregate to be used in the improved concrete which achieves a very strong bond with the cement such as Portland cement used in the concrete and is insoluble in the alkaline components of said concrete. The rock-like aggregate of the present invention will withstand many heating and cooling cycles without internal fracture. Moreover, the improved aggregate and concrete of the present invention utilizes lead and/or boron in their inexpensive oxide form without deleterious effect on the resulting strength of the concrete.

Consequently, an object of the present invention is to provide an inexpensive shielding means having unusually high attenuation efficiency with respect to a broad energy spectrum of both neutrons and gamma radiation.

Another object of the present invention is an improved concrete to be used as a shielding means for reactors.

Still another object of the present invention is a strong and durable aggregate employing oxides of such compounds as lead and boron.

Still another object of the present invention is to provide a shielding means which may be compounded with organic or inorganic plastics and easily cast into various configurations.

Other objects and advantages of the present invention will be readily apparent from the following description and examples which illustrate exemplary embodiments of the present invention.

Generally, the present invention involves an inexpensive, strong filler for inorganic or organic plastic material consisting essentially of boron oxide and lead oxide and containing about 1% to 18% boron by weight and about 1% to 70% lead by weight. In addition, a particular portion of the present invention involves a method of producing high strength concrete adapted to shield against neutrons and gamma radiation over a wide energy spectrum and containing substantial proportions of at least one member of the group consisting of lead and boron, said member being substantially insoluble in the alkaline components of said concrete. Such method involves mixing said member in the form of an oxide composition with a material adapted to insolubilize said member in said alkaline components when the resulting mixture is sintered. The resulting mixture is pressed into lumps and then fired to a temperature sufficient to at least sinter them into strong, durable, coherent rock-like masses for a time to heat said lumps throughout to said temperature. Such lumps may then be incorporated directly into the concrete or crushed to any desired size before incorporation into the concrete. Preferably, the crushed lumps are then heated in a reducing atmosphere at a temperature sufficient to form a thin film of inert material on the surfaces of said lumps. The present invention also involves the aggregate and the concrete produced by the aforementioned process.

In a preferred embodiment of the above-described methods and compositions, a granular boron oxide composition such as a sodium calcium borate (Gerstley's borate produced by the U.S. Borax Company) is mixed with a granular lead oxide composition such as litharge and the resulting mixture is pressed into lumps adapted to form an aggregate. Such lumps may contain boron in the range of about 1% to 18% by weight and lead in the range of about 1% to 70% by weight. Preferably, however, boron is present in the range of about 1% to 15% by weight and lead in the range of about 1% to 40% by weight. Such lumps may then be fired to a temperature sufficient to at least sinter them into strong, durable, coherent rock-like masses. Temperatures in the range of between 1200° F. and 1800° F. have been found satisfactory for such sintering; however, if desired, the temperature may be substantially higher to cause the particles in the mixture to fuse together rather than merely sinter together. The temperature is then maintained for a time sufficient to heat said lumps throughout to said temperature. In the case of lumps in the form of blocks one inch by six inches by six inches, such time has been found to be in the range of one-half hour to two hours. The fired lumps of appropriate size may be directly incorporated in inorganic plastic material, e.g., structural cement such as Portland cement, clay and mortar or organic plastic material, e.g., fluid polyesters, epoxy-resins, phenol-aldehyde resins, butadiene polymers and copolymers thereof with styrene, butadieneacrylonitrile copolymers, chloroprene polymers and copolymers, and vinyl halide and vinylidene halide resins, polyethylene,

butyl rubber, polyisobutylene and polyisoprene. However, where the lumps are in the form of large blocks, they must be first crushed to the desired fineness, before incorporation into the plastic material.

While the preferred aggregate may be produced as set forth above, it is preferred that the method incorporate additional steps to reduce the solubility of the aggregate components even further in the alkaline components of the concrete. One method of further reducing such solubility is the incorporation of a small amount of a sulfate compound in the granular mixture. Such sulfate compound may be incorporated simply by utilizing a lead sulfate compound in the initial formation of the mixture. Another method of incorporating such sulfate compound is by forming a paste of the granular boron oxide and the granular lead oxide composition with an aqueous sulfate solution such as sulfuric acid. Still another method of incorporating the sulfate compound in the mixture is to merely dip the pressed lump into an aqueous sulfate solution such as sulfuric acid. The wetting of the boron oxide-lead oxide composition results in an immediate physio-chemical reaction which causes the material to take an initial set and have physical properties that lend themselves well to an extrusion or pelletizing process. In addition, when the material is subsequently dried and fired the product resulting is substantially completely insoluble in the alkaline components of the concrete.

The preferred method of completely insolubilizing the boron oxide-lead oxide composition in the alkaline components of the concrete involves heating the sintered lumps in a reducing atmosphere at a temperature sufficient to form a thin film of inert material on the surface of said lumps. Preferably such treatment of the fired lumps takes place after they have been crushed to a size adapted for inclusion in the cement to form concrete. The reducing atmosphere may be achieved in a variety of ways. One way is to simply utilize the customary reducing atmosphere such as carbon monoxide and heat the crushed lumps while they are being mildly agitated in a range of from about 700° F. to 1000° F. Another way of achieving the reducing atmosphere during the heating of the crushed sintered lumps is by spraying or dipping the lumps with a liquid carbonaceous material such as glycerin or diesel oil. Such liquid carbonaceous material contains carbon in a reduced form so that the consequent heating causes mild burning on ignition. During such heating the surface portions of the crushed sintered lumps react with the carbonaceous material to form a thin film containing carbon and the components of the crushed sintered lumps in reduced form such as lead. The preferred method of obtaining the reducing atmosphere involves mixing the crushed sintered lumps with a small amount (about 2% by weight) of solid carbonaceous material such as charcoal, lamp black or coke or other form of free carbon. The resulting mixture is then mildly agitated and heated to temperatures in the range of about 700° F. to 1000° F. in the absence of excess air. At such temperatures the carbon reacts with the surface portion of the sintered crushed lumps to form a thin film of inert material and precludes the possibility of free lead oxide being present on the surface of the particle and also effectively contains any free alkali within the particle.

When the preferred aggregate of the present invention containing a mixture of boron oxide-lead oxide composition is produced by the above-described method, it has been found that the inclusion of a small percentage of feldspathic such as anorthite results in a substantial improvement in the properties of the aggregate. The amount of feldspathic material to be added will normally range about 5% to 15% by weight of the aggregate. When such feldspathic material is added it is found that the resulting aggregate is greatly strengthened and hardened and the melting point is over a wider and more easily controlled range of temperatures.

5

While the preferred aggregate of the present invention contains a mixture of lead oxide-boron oxide composition, the methods of the present invention may be utilized to produce aggregates containing only boron oxide or lead oxide compositions and said aggregate will also be substantially insoluble in the alkaline components of the concrete in which such aggregate is used. Where it is desired to utilize an aggregate containing solely a boron oxide composition, the method of the present invention involves mixing a granular boron composition with a granular feldspathic material. The boron oxide composition may be a boron frit or simply a natural boron mineral such as sodium borate. The feldspathic material may be anorthite. The granular feldspathic-boron oxide composition mixture may be pressed into lumps adapted to form an aggregate. Such lumps may then be fired at a temperature sufficient to sinter them into strong, durable, coherent rock-like masses for a time sufficient to heat said lumps throughout to said temperature. The resulting sintered lumps may then be used directly with a structural concrete such as Portland cement to form the desired shielding concrete or, if the lumps are too large in size, then they may be crushed to a size adapted for inclusion in cement concretes. The aggregate resulting from such method will consist essentially of boron oxide and a feldspathic material and contain about 1% to 18% of boron by weight.

Where it is desired to produce the aggregate of the present invention containing only lead oxide composition, such aggregate may be produced by mixing a granular lead composition such as litharge with an amount of sulfuric acid sufficient to obtain a paste and sufficient to form a film of inert material on the surface of the lead oxide particles when they are subsequently sintered. Such paste may be formed into lumps of desired size by a pelletizing or extrusion process. Such lumps are then fired to a temperature sufficient to sinter the lead oxide granules into strong, durable, coherent rock-like masses for a time sufficient to heat said lumps throughout to said temperature. The sintered lumps may then be heated in a reducing atmosphere at a temperature sufficient to form a thin film of inert material on the surfaces of said lumps. Any other suitable material may be mixed into the paste of lead oxide and the aqueous sulfate solution such as sodium carbonate. The aggregate produced by such method may contain about 1% to 70% by weight of lead.

The following specific examples will serve to illustrate the invention and to make clear the manner in which it may be practiced.

#### EXAMPLE I

Litharge (PbO) and sodium calcium borate (Gerstley's borate) were mixed together in granular form to form a mixture containing approximately 30% lead and 10% boron by weight. Prior to mixing, the sodium calcium borate was heated to drive off its water of crystallization and to attain an anhydrous condition. The mixture of litharge and sodium calcium borate was then fired at a temperature of about 1500° F. for approximately one hour. The resulting product had a specific gravity of approximately 3.2 to 3.5 and formed a very hard, very dense opaque material in which the solubility of the components was substantially reduced when the sintered mixture was subsequently used to form a concrete.

#### EXAMPLE II

A filler, produced as described in Example I, was mixed with polyethylene after the polyethylene was heated to above its melting point. The mixture consisted of 64% by weight of the product of Example I crushed to pass through a 300 mesh screen and 36% by weight of polyethylene. A homogeneous dispersion was easily obtained since the product of Example I was wetted by the liquid polyethylene.

6

#### EXAMPLE III

An aggregate was produced as described in Example I except that the litharge-sodium borate mixture was formed into a paste by the inclusion of a 10% solution of sulfuric acid prior to firing. The product when fired showed a complete solution of the solubility problem in concrete.

#### EXAMPLE IV

The leaded-borate aggregate produced by the process described in Example I was dipped into a glycerin bath and permitted to stand for several hours. The aggregate was then roasted at a temperature sufficient to volatilize and burn off the glycerin leaving a dark colored residual surface on the aggregate. Upon subsequent incorporation in a concrete it was found that the aggregate was completely insoluble in the alkaline components of said concrete.

#### EXAMPLE V

The aggregate as produced in Example I was crushed and then mixed with a small amount of charcoal (about 2% by weight of the aggregate) and then heated during mild agitation to a temperature of about 850° F. It was found that even though the exterior surfaces of the aggregate particles may fuse that there was no tendency for the particles to stick together since they were apparently separated by the free carbon dust. After treatment the aggregate was then mixed with Portland cement to form a concrete and was found to be completely insoluble in the alkaline components of said concrete.

#### EXAMPLE VI

A granular mixture of 75% boron frit (approximate boron frit composition by weight:  $\text{SiO}_2$ —20.00%,  $\text{Al}_2\text{O}_3$ —10.00%,  $\text{CaO}$ —15.00%,  $\text{B}_2\text{O}_3$ —55.00% and  $\text{Fe}_2\text{O}_3$ —0.08%) and 25% anorthite were mixed together and pressed into brick form. The resulting bricks contain approximately 10% by weight of elemental boron. Bricks were then subsequently fired at a temperature from about 1300° F. to 1450° F. for a period of approximately one and one-half hours. The resulting product was a very strong and very durable opaque rock-like mass which formed an excellent crushed aggregate for a Portland cement. The aggregate was then incorporated into a Portland cement concrete and found to be substantially insoluble in the alkaline component of said concrete.

It should be noted that when the insolubilization of the aggregate is achieved by the use of a sulfate material such sulfate material may be added either as an aqueous solution of a sulfate such as sulfuric acid or calcium sulfate or it may be added initially in the form of lead sulfate. Likewise, if desired, the sulfate concentration in the aggregate may be achieved by the addition of any sulfur-containing composition and the sulfate generated during the sintering step of the process. Also, if desired, a portion of the lead and/or boron may be included in its elemental form.

One of the main features of the present invention is the production of an aggregate which, although it may contain large percentages of a boron oxide composition or a lead oxide composition, or both, still achieves a strong bond with the Portland cement used in the formulation of concretes. The rock-like aggregate of the present invention does not exhibit any solubility in the alkaline components of the concrete. Consequently, the customary salts or gels which form at surfaces of particles normally containing boron oxide compositions or lead oxide compositions do not form to weaken the bond between the matrix and the aggregate. This feature of the present invention appears to result from the formation of a film on the surface of the aggregate particles of inert material. Such film apparently contains reduced form of the components of the aggregate combined with carbon. Also, the free alkalis which are normally present within the

aggregate are effectively contained by such film and bound within the particle.

Another feature of the present invention is the unexpected substantially increased attenuation efficiency achieved by its composition and the concrete produced therefrom. The concrete of the present invention contains a substantially larger oxygen content than the ordinary concrete of the prior art or the concrete produced by Borst. Since the aggregate and the concrete of the present invention contain large quantities of heavy elements, intermediate elements and lighter elements, it constitutes a very good shield for neutrons and gamma radiation over a wide energy spectrum. As shown below in Tables I and II, the concrete of the present invention is much more effective than regular concrete against low energy neutrons and gamma rays and even better than lead on a weight basis.

Table I.—Neutron attenuation

|                                     | Attenuation length for<br>thermal neutrons, Cm. |
|-------------------------------------|-------------------------------------------------|
| Conventional concrete -----         | Approx. 75.0                                    |
| Concrete of present invention ----- | 0.4                                             |

Table II.—Weight of material producing equal shielding characteristics against 0.6 mev. gamma rays

| Material:                           | Weight (lbs.) |
|-------------------------------------|---------------|
| Lead -----                          | 84.7          |
| Conventional concrete -----         | 133           |
| Concrete of present invention ----- | 62.0          |

It will be understood that the foregoing description and examples are only illustrative of the present invention and it is not intended that the invention be limited thereto. Many other specific embodiments of the present invention will be obvious to one skilled in the art in view of this disclosure. All substitutions, alterations and modifications of the present invention which come within the scope of the following claims or to which the present invention is readily susceptible without departing from the spirit and scope of this disclosure are considered part of the present invention.

I claim:

1. A high strength concrete adapted to shield against neutrons and gamma radiation over a wide energy spectrum consisting essentially of a structural cement and an aggregate comprising sintered, strong, rock-like masses containing between about 1% to 70% lead by weight in the form of lead oxide and about 1% to 18% boron by weight in the form of boron oxide, said aggregate being substantially insoluble in the alkaline components of said cement.

2. A method of producing strong, rock-like aggregate for use in hydraulic cement concrete adapted to shield against neutrons and gamma radiation over a wide energy spectrum, said aggregate being substantially inert and insoluble in alkaline components of such concrete where-

by the strength and stability of concrete containing such aggregate is not impaired, comprising:

(a) mixing a granular boron oxide composition and a granular lead oxide composition in proportions adapted to form a mixture containing between 1 percent and 15 percent of boron and 1 percent to 40 percent of lead;

(b) forming said mixture into bodies; and

(c) heating said formed bodies to a temperature and for a time sufficient to sinter the bodies into strong rock-like masses thereby insolubilizing the compositions in alkaline components of hydraulic cement, but adapted to firmly bond therewith.

3. In a method as stated in claim 2 the step of adding granular feldspathic material to the mixture before forming the mixture into bodies.

4. A method as stated in claim 2 wherein said bodies are heated in a reducing atmosphere to form a thin film of inert material on said rock-like masses.

5. A method as stated in claim 2 wherein an aqueous sulfate solution is added to said compositions before forming them into bodies.

6. A method of producing a strong aggregate for use in hydraulic cement concrete adapted to shield against neutrons and gamma radiation over a wide energy spectrum,

(a) mixing sodium calcium borate and litharge in proportions adapted to form a mixture containing between 1 percent and 15 percent of boron and between 1 percent and 40 percent of lead, on a dry basis;

(b) forming said mixture into bodies;

(c) heating said formed bodies to a temperature and for a time sufficient to sinter the bodies into strong, rock-like masses thereby insolubilizing the compositions in alkaline components of hydraulic cement.

7. A strong, rock-like aggregate for use in curable matrix, said aggregate being adapted to shield against neutrons and gamma radiation over a wide energy spectrum, comprising sintered masses composed of a mixture of sodium calcium borate and litharge, said masses containing between 1 percent and 15 percent of boron and between 1 percent and 20 percent of lead, said aggregate being virtually insoluble in alkaline components of hydraulic cement.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

|           |         |                    |         |
|-----------|---------|--------------------|---------|
| 2,063,329 | 12/1936 | Morrison.          |         |
| 2,607,700 | 8/1952  | Vail -----         | 109—97  |
| 2,726,339 | 12/1955 | Borst.             |         |
| 3,010,840 | 11/1961 | Goff -----         | 106—47  |
| 3,126,351 | 3/1964  | Blair et al. ----- | 252—478 |

CARL D. QUARFORTH, *Primary Examiner.*

OSCAR R. VERTIZ, *Examiner.*