

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C04B 7/60, 7/42	A1	(11) International Publication Number: WO 97/09281 (43) International Publication Date: 13 March 1997 (13.03.97)
(21) International Application Number: PCT/US96/14346 (22) International Filing Date: 6 September 1996 (06.09.96) (30) Priority Data: 60/003,475 8 September 1995 (08.09.95) US (71) Applicant: FMC CORPORATION [US/US]; 1735 Market Street, Philadelphia, PA 19103 (US). (72) Inventors: STOKES, David, B.; 501 Richards Drive, Shelby, NC 28150 (US). FOLTZ, Gary, E.; 230 Mockingbird Lane, McAdenville, NC 28101 (US). MANISSERO, Claudio, E.; 4026 Biggerstaff Road, Maiden, NC 28650 (US). (74) Agents: LINKER, Raymond, O., Jr. et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CEMENT COMPOSITIONS FOR CONTROLLING ALKALI-SILICA REACTIONS IN CONCRETE AND PROCESSES FOR MAKING SAME (57) Abstract Processes for making cement which when used to make concrete can stabilize the concrete against alkali-silica reactivity (ASR) from alkali containing components. The process includes adding lithium containing materials in the front of a cement kiln along with the cement starting materials in an amount sufficient to minimize ASR.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**CEMENT COMPOSITIONS FOR CONTROLLING ALKALI-SILICA
REACTIONS IN CONCRETE AND PROCESSES FOR MAKING SAME**

Cross-Reference to Related Applications

This application is related to commonly owned
copending Provisional Application Serial No.
60/003,475, filed September 8, 1995.

5 Field of the Invention

This invention relates generally to cement
compositions and processes for producing the same, and
more particularly cement for controlling alkali-silica
reaction in concrete which includes the cement as a
10 component.

Background of the Invention

Concrete is a conglomerate of aggregate (such
as gravel, sand, and/or crushed stone), water, and
hydraulic cement (such as portland cement), as well as
15 other components and/or additives. Concrete is
generally fluidic when it is first made, enabling it to
be poured or placed into shapes, and then later
hardens, and is never again fluidic, in the general
sense. Typically, moisture present in normal concrete
20 is basic (that is, has a high pH). Alkali materials
can be supplied by the cement, aggregate, additives,
and even from the environment in which the hardened
concrete exists (such as salts placed on concrete to
melt ice).

25 Silica compounds are typically found in the
aggregate components of concrete. Silica which is
present in aggregates used to make concrete and mortars
is subject to attack and dissolution by hydroxide ions

-2-

present in basic solutions. Generally, the higher the pH (i.e., the more basic the solution), the faster the attack.

Different forms of silica show varying
5 degrees of susceptibility to this dissolution. If there is sufficient alkali metal ion also present in this solution (such as sodium or potassium ions), the alkali metal ions can react with the dissolved silica and form an alkali-silica gel. Under certain
10 conditions, the resultant alkali-silica gel can absorb water and swell. The swelling can exert pressures greater than the tensile strength of the concrete and thus cause the concrete to swell and crack. This process (hydroxide attack of silica, followed by
15 reaction with alkali such as sodium and potassium) is referred to generally in the art as an "alkali-silica reaction" or "ASR".

ASR has caused the failure of concrete structures, although rarely. Further, ASR can weaken
20 the ability of concrete to withstand other forms of attack. For example, concrete that is cracked due to this process can permit a greater degree of saturation and is therefore much more susceptible to damage as a result of "freeze-thaw" cycles. Similarly, cracks in
25 the surfaces of steel reinforced concrete can compromise the ability of the concrete to keep out salts when subjected to deicers, thus allowing corrosion of the steel it was designed to protect.

ASR is a common chemical process in many
30 concretes around the world. As an indication of its importance to the concrete industry, by 1991 over 1,450 research articles had been published on the subject. See S. Diamond, *Alkali-aggregate reactions in concrete: an annotated bibliography 1939-1991*, Washington, D.C.:
35 National Research Council, Strategic Highway Research Program, SHRP-C/UWP-92-601:470 (1992).

-3-

In 1987, Congress authorized a \$150 million, five-year research program to be administered by the National Research Council to study and develop improvements in highway construction materials and construction practices. This program was called the Strategic Highway Research Program (SHRP). One of the areas addressed by this program was ASR mitigation. Four recommendations resulted from the SHRP research for preventing ASR in concrete. D. Stark, et al., *Eliminating or minimizing alkali-silica reactivity*, Washington, D.C.:National Research Council, Strategic Highway Research Program, SHRP-C-343 (1993) (the "SHRP report").

One recommendation was the use a low alkali cement, which is defined as a cement with a sodium equivalent of 0.60% or less. The sodium equivalent of a cement is the weight percent of sodium, reported as sodium oxide, plus 0.658 times the weight percent of potassium, reported as potassium oxide. Sodium equivalent (Na_2O_e) can be represented generally by the formula $\text{NaO}_2 + 0.658 \times \text{K}_2\text{O} = \text{Na}_2\text{O}_e$.

While the use of a low alkali cement can have some effectiveness, it is not a guarantee of ASR prevention. Low alkali cement is not always available on a local basis, can have limited availability, and can be more expensive than high alkali cement. Further, if the raw feed for the cement production contains high levels of alkali, then the production of low alkali cement from such feed can generate much greater waste than would otherwise be the case. Generally, "fines" are a waste product of cement production and are normally recirculated into the cement kiln. However, when the raw feed has a high alkali level, the fines must be removed from the process to make a low alkali cement and constitute a waste material. These fines are generally referred in the industry as cement kiln dust.

-4-

Still further, using a low alkali cement is no guarantee of ASR control, as the cement is not the sole source of the alkalies in concrete that can contribute to the problem. Alkalies also can be
5 supplied by pozzolans that are either admixed in or part of the blended cement. Alkalies can be supplied by the mix water, admixtures used in the concrete, the aggregate itself, including recycled concrete used as aggregate, and/or deicers applied in snow and ice
10 removal.

Another recommendation set forth by the SHRP report is the use a non-reactive aggregate. This, however, is not always possible. There are limited aggregates with no potential for reactivity, since all
15 silica has some potential for reaction and most aggregates contain significant amounts of silica. Recycled concrete when used as aggregate can also be reactive, particularly if it had already had ASR occurring before it was recycled. There are
20 environmental reasons to use recycled glass as aggregate, but this is very reactive material. Also, transporting aggregates over long distances instead of using locally available materials adds significantly to the cost of concrete production.

Another recommendation is the use of appropriate levels of a suitable pozzolan. A pozzolan is a siliceous material that can combine with lime and water to harden, similar to a cement with just water. Since the hydration of cement produces lime as a
25 byproduct (resulting in its basic nature), pozzolans can work well with cements. The pozzolan may be added as a mineral admixture at the time of concrete production, blended with the cement, or interground with the cement during the final production step of
30 cement. The end result is about the same, as neither the cement nor the pozzolan is substantially changed as a result of the blending.

-5-

However, sources of suitable pozzolans are not always available locally, and the supplies are limited. Also, many pozzolans used for this purpose are waste products, and thus are quite variable in composition. An example is fly ash, which is the end result of coal burned for electric generation.

Further, sufficient amounts of the pozzolan must be used, or the protection is short lived, or the ASR can actually be made worse. This is particularly true of pozzolans with significant lime contents (>10%), such as many fly ashes. In a cementitious system, the Ca:Si ratio is very important to its stability with regard to ASR. The higher the Ca:Si ratio, the less capable the system is of tying up alkali present. Thus the protection against ASR is less with high lime fly ashes. A low lime content pozzolan (<10%) will reduce the ratio and give more protection from increased alkalies. However, a high lime content pozzolan will not give this protection, and further, since pozzolans carry their own alkalies into the system, this can easily make the situation worse.

Still another recommendation is the use a lithium-based admixture. Use of lithium was shown to be effective in ASR inhibition in 1951 (see W.J. McCoy and A.G. Caldwell, "New approach to inhibiting alkali-aggregate expansion," *J.Amer.Concrete Institute*, 22:693-706 (1951)). See also Y. Sakaguchi, et al., "The inhibiting effect of lithium compounds on alkali-silica reaction," *Proceedings, 8th international conference, alkali aggregate reaction*, Kyoto, Japan: 229-234 (1989), and the SHRP report.

Lithium salts, such as lithium hydroxide monohydrate, have been added to cement at the grinding stage of the cement production. J. Gajda, *Development of a cement to inhibit alkali-silica reactivity*, Skokie, IL, Portland Cement Association Research and

-6-

Development Bulletin RD115T (1996). As with the pozzolan blended cements mentioned above, the net effect is basically the same as if the lithium salt were admixed into the concrete separately at the time the concrete was batched. That is, by adding the lithium salt to the cement at the time of grinding, neither the cement nor the lithium salt is changed during the process. Rather, the lithium salt and cement are merely blended.

One problem associated with adding lithium salts to the concrete mixture or grinding lithium salts with cement is that substantial amounts of the lithium (about 50%, as reported in the SHRP Report) are "locked up" in the hydration products of the early hydration reactions of the cement. A substantial portion of the lithium ions, therefore, is unavailable for use in controlling ASR. This generally happens within the first few days of hydration. Still further, the concentration of hydroxyl ion can increase when lithium salts are admixed into concrete and mortars (see the SHRP Report). This can make the job of the lithium ion that much more difficult, and requires more lithium than would otherwise be the case.

Summary of the Invention

The present invention provides a process for producing cement which, when used to make concrete or mortar mixtures, can inhibit alkali-silica reactivity from alkali containing components. In the invention, lithium containing materials, including lithium salts, lithium ores, lithium ore concentrates, and preheated or decrepitated lithium ore and concentrates, are heated in a cement kiln with cement starting materials (ores) to form cement clinker. The lithium containing material supplies lithium ions to the cement, which enables the cement thus produced to inhibit alkali-silica reaction in concrete and mortars made with the

-7-

cement. This in turn can minimize and/or prevent deterioration of concrete from ASR.

The process of the invention also can result in reduced energy requirements necessary to manufacture the cement for a given unit of cement because lithium can act as a flux in cement production. Further, lithium containing materials include siliceous materials which are pozzolanic by nature. In addition, when lithium bearing ores are used as the lithium source, the process of the invention can provide economic advantages as compared to lithium salts (which require extracting and purifying lithium from the ores). Still further, less lithium is required to inhibit ASR in the resultant concrete than purified forms of lithium, because lithium present in lithium bearing ores can be more slowly released into the concrete mixture after much of cement hydration has occurred, in contrast to lithium salts.

The present invention also includes cement produced according to the invention, as well as concrete and mortar which include the cement as a component.

Brief Description of the Drawings

Some of the features and advantages of the invention having been described, others will become apparent from the detailed description which follows, and from the accompanying drawings, in which:

Figure 1 is an x-ray diffraction pattern of clinker prepared at 1400°C without lithium;

Figure 2 is an x-ray diffraction pattern of clinker prepared at 1300°C with lithium; and

Figure 3 is a graph illustrating isothermal calorimetry of clinker made with and without lithium at 1400°C.

Detailed Description of the Invention

Cement is manufactured by introducing cement starting materials into a kiln and heating the cement starting materials to extremely high temperatures, typically about 2700°F. Cement starting materials typically include carbonates (limestone or chalk), silica, clays, shales, slates and the like and mixtures thereof. As the skilled artisan will appreciate, other starting materials can also be used. This stage is referred to generally in the art as "clinkering" and the resultant product is referred to as "clinker." The clinker is then cooled and ground, typically with gypsum to control the quick setting properties of the aluminate phases in the cement.

In the present invention, lithium containing materials are added with the cement starting materials in the front end of the cement kiln and heated with the cement starting materials to form clinker. The resultant cement product (or clinker) thus includes lithium and can be an effective mitigator of ASR when added to a concrete or mortar mixture.

As used herein, the term "cement" refers to, but is not limited to, hydraulic and alite cements, such as Portland cement; blended cements, such as Portland cement blended with fly ash, blast-furnace slag, pozzolans, and the like, and mixtures thereof; masonry cement; oil well cement; natural cement; alumina cement; expansive cements, and the like, and mixtures thereof.

Exemplary lithium containing materials include, but are not limited to, refined lithium products such as lithium salts (for example, lithium carbonate, lithium hydroxide monohydrate, lithium nitrate, lithium fluoride, lithium chloride, and the like, and mixtures thereof). Other lithium sources include lithium bearing ores and lithium ore concentrates such as lithium aluminum silicates, such

-9-

as spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$), petalite
($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$), eucryptite ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$),
montrebrasite, lepidolite, lithium-aluminate phosphate
ores, such as amblygonite ($\text{LiF} \cdot \text{AlPO}_4$), lithium-bearing
5 clays, and the like and mixtures thereof. As the
skilled artisan will appreciate, the term "lithium
bearing ore concentrate" refers to lithium bearing ores
which have been treated (beneficiated) to concentrate
the lithium bearing mineral. For ease of reference, as
10 used herein the term "lithium bearing ores" refers to
both beneficiated and non-beneficiated lithium bearing
ores.

The lithium containing material is added to
the cement raw feed in the front end of the kiln in an
15 amount effective to mitigate the detrimental effects of
ASR in concrete manufactured using the resultant cement
product. In the present invention, the lithium
containing material is added to the raw feed in an
amount sufficient to provide a molar ratio of lithium
20 to sodium equivalent ($\text{Na}_2\text{O}_e = \text{NaO}_2 + 0.658 \times \text{K}_2\text{O}$) in the
resultant clinker between about 0.1:1 to about 10:1,
preferably about 1:10 to about 5:1, and more preferably
about 0.5:1 to about 2:1.

In addition, in the present invention, cement
25 clinkers can be formed at lower kiln temperatures than
conventionally used. Typically, clinker is formed in
cement kilns at temperatures of about 1420°C to about
 1450°C . In contrast, in the present invention,
clinkering can take place at reduced temperatures of
30 about 1300°C to about 1420°C . This is believed to
result from the flux effect of the lithium containing
compounds when added to the front end of a cement kiln.

Conventional clinkering processes typically
require a large amount of energy to decompose these
35 materials so that they can react to form the basic
constituents of cement. Addition of lithium containing
materials to the front end of the cement kiln also can

-10-

result in reduced energy requirements for the clinkering process (about 1% to about 3% less energy required, as compared to the energy required to produce similar units of cement without lithium containing materials). This can, in turn, result in reduced energy costs, fuel costs, and the like. This can have favorable environmental implications since less fuels need to be consumed to manufacture the same amount of cement, with the concurrent reduction in pollutants.

10 This can also increase the life of refractory bricks which line cement kilns per given unit of cement produced. Still further, because less energy is required, this can result in shorter kiln residence times and increased production rates.

15 To demonstrate that the lithium materials do not interfere with the formation of the clinker minerals at the levels that they would typically be used for ASR inhibition, and that clinker can form at lower temperatures, x-ray diffraction was used to

20 characterize cement clinkers made with and without lithium containing materials. Figure 1 is an x-ray diffraction pattern of clinker (with gypsum) produced from a raw feed material (or raw meal) burned at 1400°C for 4 hours without lithium. The oxide concentrations

25 of the raw feed are given below in Example 1. The following peaks are labelled in Figure 1: Alite (labelled "A" in Figure 1), Belite ("B"), C₃A ("C"), F ("C₄AF") and L ("lime"). Alite refers to tricalcium silicate (C₃S); Belite refers to dicalcium silicate

30 (C₂S); C₃A refers to tricalcium aluminate; and C₄AF refers to tetracalcium aluminoferrite.

Figure 2 is an x-ray diffraction pattern of clinker (with gypsum) produced from the same raw feed material (or raw meal) as in Figure 1, but which also

35 included spodumene ore concentrate. The spodumene ore was added to the raw feed in an amount sufficient to provide about 0.51% Li₂O in the clinker. The raw feed

-11-

material plus the lithium ore was burned at 1300°C for 4 hours. The labels A, B, C, F and L have the same meaning as in Figure 1.

As shown in Figure 2, when lithium was
5 present, no new peaks were formed, and only subtle differences in intensities were present. The fact that there is no difference in the locations of the main peaks demonstrates that the phases present are essentially the same. Further, Figure 2 demonstrates
10 that clinker is formed at about 1300°C.

Hydration calorimetry of ground powders from clinkers made with and without lithium bearing materials also give very similar results. Figure 3 is a graph illustrating isothermal calorimetry properties
15 at 38°C of clinker made with and without lithium. "A" represents the hydration properties of clinker made from raw feed of the same composition as described above with regard to Figure 1 (without lithium); "B" represents the hydration properties of clinker made
20 from raw feed of the same composition as described above with regard to Figure 2, with lithium, except that the lithium carbonate was added in an amount sufficient to provide 0.75% Li₂O in the clinker. Both clinkers were produced from materials burned at 1400°C
25 for four hours.

As illustrated in Figure 3, there is also some increased and earlier hydration with added lithium. This demonstrates greater hydraulic activity of the clinker prepared with lithium containing
30 materials. Because of the greater hydraulic activity of the cement made with lithium in accordance with the present invention, the resultant cement does not need to be ground as fine as would otherwise be the case for equivalent rate of reaction, resulting in a further
35 reduction in production costs.

The present invention is also useful for making high alkali cement which also is capable of

-12-

stabilizing concrete against alkali-silica reactivity. High alkali cement is generally defined as cement having a sodium equivalent (as defined above) of about 0.60% or greater. However, some standards require that

5 low alkali cement have a sodium equivalent of about 0.40% or less. In such circumstances, high alkali cement also can be defined as cement having a sodium equivalent of about 0.40% or greater.

As discussed above, if the raw feed for the

10 cement production contains high levels of alkali, then the production of low alkali cement (less than about 0.60% sodium equivalent) from such feed can generate much greater waste than would otherwise be the case. Generally, cement production generates "fines" or

15 cement kiln dust. Fines are a waste product of cement production and are normally recirculated into the cement kiln. However, when the raw feed has a high alkali level, the fines must be removed from the process to form low alkali cement, and thus constitute

20 a waste material.

Thus, prior techniques require the removal of fines from the cement making process when using high alkali cement starting materials to provide low alkali cement. In this aspect of the invention, lithium

25 containing materials are added in the front end of the kiln along with high alkali starting materials. In contrast to prior techniques, because of the ASR mitigating properties imparted to the cement by the lithium containing materials, the fines do not have to

30 be removed. Rather, the fines can be recirculated in the kiln. Although the resultant cement can be a high alkali cement, the use of the lithium containing materials in the front end of the kiln results in a high alkali cement with ASR mitigating properties.

35 This can provide process advantages, i.e., eliminate the need for removing fines. This also can have favorable environmental implications, i.e., a

-13-

reduction in fines as a hazardous waste which must be properly disposed of.

The present invention also provides lithium containing cements useful for making concrete and mortar resistant to alkali-silica reactivity from alkali containing components. The concrete compositions generally include cement, aggregate, and water. The cement is present in the fluid concrete mixture in an amount between about 5% to about 20% by weight based on the total weight of the concrete mixture.

Aggregates can include, but are not limited to natural and crushed quarried aggregate, sand, recycled concrete aggregate, glass, and the like, as well as mixtures thereof. Aggregate is present in the fluid concrete mixture in an amount between about 75% to about 95% by weight, based on the total weight of the concrete mixture.

The fluid concrete mixture also includes water, in an amount ranging from about 2% to about 10% by weight based on the total weight of the mixture. The fluid concrete mixture also can include other materials as known in the art for imparting various properties to concrete, including, but not limited to, air-entraining admixtures, water reducing admixtures, accelerating admixtures, pozzolans, such as, but not limited to, fly ash, metakaolin, and silica fume, and the like. These agents can be present in conventional amounts.

Although reference has been made to the components of concrete, it will be appreciated that the present invention also includes mortar compositions, which generally are similar in composition to concrete, except that mortar is typically made with sand as the sole aggregate, in contrast to concrete which includes larger aggregates. Sand in this sense is aggregate of 3/8" and smaller diameter.

-14-

The present invention will be further illustrated by the following non-limiting examples.

Example 1

Making an ASR Resistant

Cement with Spodumene Ore Concentrate

In this example, the target is a Li_2O content of 0.51% by weight in the clinker, which would be sufficient for a high degree of ASR.

The constituents of a mixture of cement starting materials (60.5% raw feed, 30.9% calcium carbonate, 0.2% silica), and 8.5% spodumene ore concentrate are given below, along with the clinker composition that would result from the use this mixture:

Oxide	Raw Feed	Ore Concentrate	Clinker
SiO_2	21.74	59.5	21.25
Al_2O_3	5.75	24.1	6.39
CaO	66.33	2.30	66.66
Fe_2O_3	3.48	2.30	2.66
MgO	2.96	0.70	2.14
Na_2Oeq	1.20	1.70	1.01
Li_2O	0	5.20	0.51

Figure 2 is an x-ray diffraction pattern of the resultant clinker of this example.

Example 2

Making an ASR Resistant

Cement with Lithium Carbonate

In this example, 0.1% to 10% Li_2CO_3 by weight of the combined ingredients was added to a raw feed as described above in Example 1 into the kiln.

Example 3

Making an ASR Resistant

Cement with Lithium Hydroxide

In this example, 0.1% to 10% $\text{LiOH}\cdot\text{H}_2\text{O}$ by weight of the combined ingredients was added to a raw feed as described above in Example 1 into the kiln.

-15-

Example 4
Making an ASR Resistant Cement with
Decrepitated Spodumene Ore Concentrate

In this example, the target is a Li_2O content of 0.42% by weight in the clinker, which would be sufficient for moderately high degree of ASR.

The constituents of a mixture of cement starting materials (64.7% raw feed, 38.2% calcium carbonate, 0.2% silica), and 7.0% decrepitated spodumene ore concentrate are given below, along with the clinker composition that would result:

	Oxide	Raw Feed	Ore Concentrate	Clinker
	SiO_2	21.74	59.5	21.00
	Al_2O_3	5.75	24.1	6.17
15	CaO	66.33	2.30	67.14
	Fe_2O_3	3.48	2.30	2.75
	MgO	2.96	0.70	2.24
	Na_2Oeq	0.8	1.70	0.73
	Li_2O	0	5.20	0.42

The foregoing examples are illustrative of the present invention and are not to be construed as limiting thereof.

THAT WHICH IS CLAIMED IS:

1. A process for making cement capable of stabilizing concrete against alkali-silica reactivity (ASR) from alkali containing components, the process comprising heating cement starting materials and
5 lithium containing materials in an amount sufficient to minimize ASR in concrete under conditions sufficient to chemically react the cement starting materials to form cement clinker.
2. The process of Claim 1, further
10 comprising grinding the cement clinker.
3. The process of Claim 1, wherein said lithium bearing material comprises lithium bearing ore.
4. The process of Claim 3, wherein said lithium bearing ore is selected from the group
15 consisting of spodumene, petalite, eucryptite, amblygonite, montrebrasite, lepidolite, lithium-bearing clays, and mixtures thereof.
5. The process of Claim 3, wherein said lithium bearing ore is decrepitated lithium bearing
20 ore.
6. The process of Claim 1, wherein said lithium bearing material comprises lithium salt.
7. The process of Claim 6, wherein said lithium bearing salt is selected from the group
25 consisting of lithium carbonate, lithium hydroxide monohydrate, lithium nitrate, lithium fluoride, lithium chloride, and mixtures thereof.

-17-

8. The process of Claim 1, wherein said lithium containing material is present in said cement starting materials in an amount sufficient to provide a molar ratio of lithium to sodium equivalent in the resultant cement clinker between about 0.1:1 to about 10:1.

9. The process of Claim 8, wherein said lithium containing material is present in said cement starting materials in an amount sufficient to provide a molar ratio of lithium to sodium equivalent in the resultant cement clinker between about 1:10 to about 5:1.

10. The process of Claim 9, wherein said lithium containing material is present in said cement starting materials in an amount sufficient to provide a molar ratio of lithium to sodium equivalent in the resultant cement clinker between about 0.5:1 to about 2:1.

11. The process of Claim 1, further comprising prior to said heating step the step of mixing said lithium containing materials with said cement starting materials.

12. The process of Claim 1, further comprising adding said lithium containing materials to said cement starting materials during said heating step.

13. The process of Claim 1, wherein said heating step comprises heating said cement starting materials and said lithium containing materials at a temperature between about 1300°C and about 1420°C.

-18-

14. The process of Claim 1, wherein said heating step requires about 1% to about 3% less energy per unit of cement clinker produced than heating without lithium containing materials.

5 15. A process for making cement capable of stabilizing concrete against alkali-silica reactivity (ASR) from alkali containing components, the process comprising heating cement starting materials and lithium bearing ores in an amount sufficient to
10 minimize ASR in concrete under conditions sufficient to chemically react the cement starting materials to form cement clinker.

 16. A process for making cement capable of stabilizing concrete against alkali-silica reactivity
15 (ASR) from alkali containing components, the process comprising heating cement starting materials and lithium salts in an amount sufficient to minimize ASR in concrete under conditions sufficient to chemically react the cement starting materials to form cement
20 clinker.

 17. Cement produced according to the process of Claim 1.

 18. Cement produced according to the process of Claim 15.

25 19. Cement produced according to the process of Claim 16.

 20. A process for making concrete stabilized against alkali-silica reactivity (ASR) from alkali containing components, the process comprising mixing
30 cement, aggregate, and water, said cement produced by heating cement starting materials and lithium

-19-

containing materials in an amount sufficient to minimize ASR in concrete under conditions sufficient to chemically react the cement starting materials.

21. The process of Claim 20, wherein said
5 lithium bearing material comprises lithium bearing ore.

22. The process of Claim 21, wherein said lithium bearing ore is selected from the group consisting of spodumene, petalite, eucryptite, amblygonite, montrebrasite, lepidolite, lithium-bearing
10 clays, and mixtures thereof.

23. The process of Claim 21, wherein said lithium bearing ore is decrepitated lithium bearing ore.

24. The process of Claim 20, wherein said
15 lithium bearing material comprises lithium salt.

25. The process of Claim 24, wherein said lithium bearing salt is selected from the group consisting of lithium carbonate, lithium hydroxide monohydrate, lithium nitrate, lithium fluoride, lithium
20 chloride, and mixtures thereof.

26. The process of Claim 20, wherein said lithium containing material is present in said cement starting materials in an amount sufficient to provide a molar ratio of lithium to sodium equivalent in the
25 resultant cement clinker between about 0.1:1 to about 10:1.

27. The process of Claim 26, wherein said lithium containing material is present in said cement starting materials in an amount sufficient to provide a
30 molar ratio of lithium to sodium equivalent in the

-20-

resultant cement clinker between about 1:10 to about 5:1.

28. The process of Claim 27, wherein said lithium containing material is present in said cement starting materials in an amount sufficient to provide a molar ratio of lithium to sodium equivalent in the resultant cement clinker between about 0.5:1 to about 2:1.

29. Concrete produced according to the process of Claim 20.

30. A process for making concrete stabilized against alkali-silica reactivity (ASR) from alkali containing components, the process comprising mixing cement, aggregate, and water, said cement produced by heating cement starting materials and lithium bearing ores in an amount sufficient to minimize ASR in concrete under conditions sufficient to chemically react the cement starting materials.

31. Concrete produced according to the process of Claim 30.

32. A process for making concrete stabilized against alkali-silica reactivity (ASR) from alkali containing components, the process comprising mixing cement, aggregate, and water, said cement produced by heating cement starting materials and lithium bearing salt in an amount sufficient to minimize ASR in concrete under conditions sufficient to chemically react the cement starting materials.

33. Concrete produced according to the process of Claim 32.

-21-

34. A process for making high alkali cement capable of stabilizing concrete against alkali-silica reactivity (ASR) from alkali containing components, the process comprising heating cement starting materials having a high alkali content and lithium containing materials in an amount sufficient to minimize ASR in concrete under conditions sufficient to chemically react the cement starting materials to form cement clinker.

35. A process for making cement capable of stabilizing concrete against alkali-silica reactivity (ASR) from alkali containing components, the process comprising heating in a cement kiln high alkali content cement starting materials and lithium containing materials in an amount sufficient to minimize ASR in concrete under conditions sufficient to chemically react the cement starting materials to form high alkali cement clinker, wherein said heating step results in the production of cement kiln dust, and wherein said process further comprises recirculating said cement kiln dust in the cement kiln.

1/3

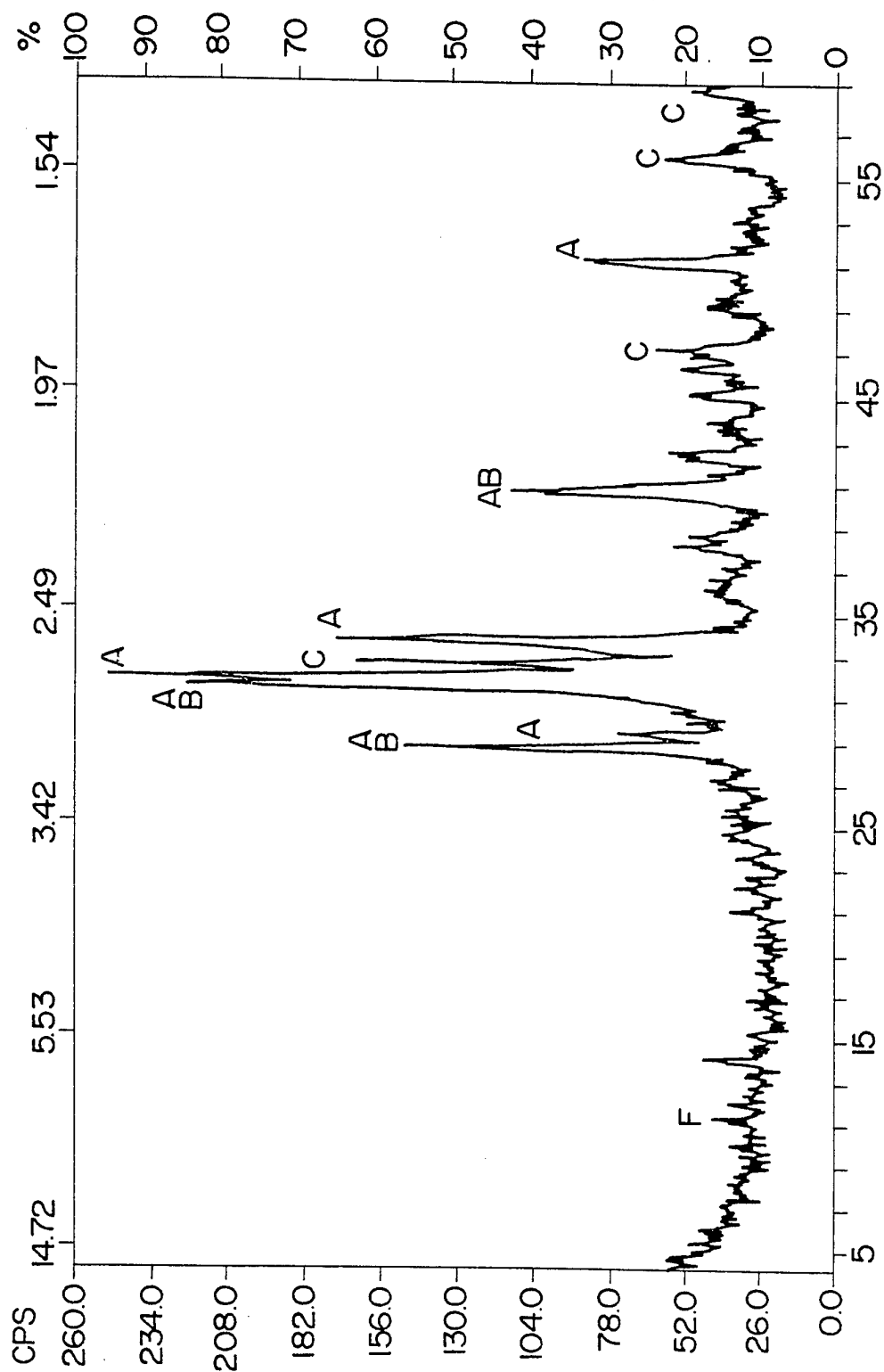
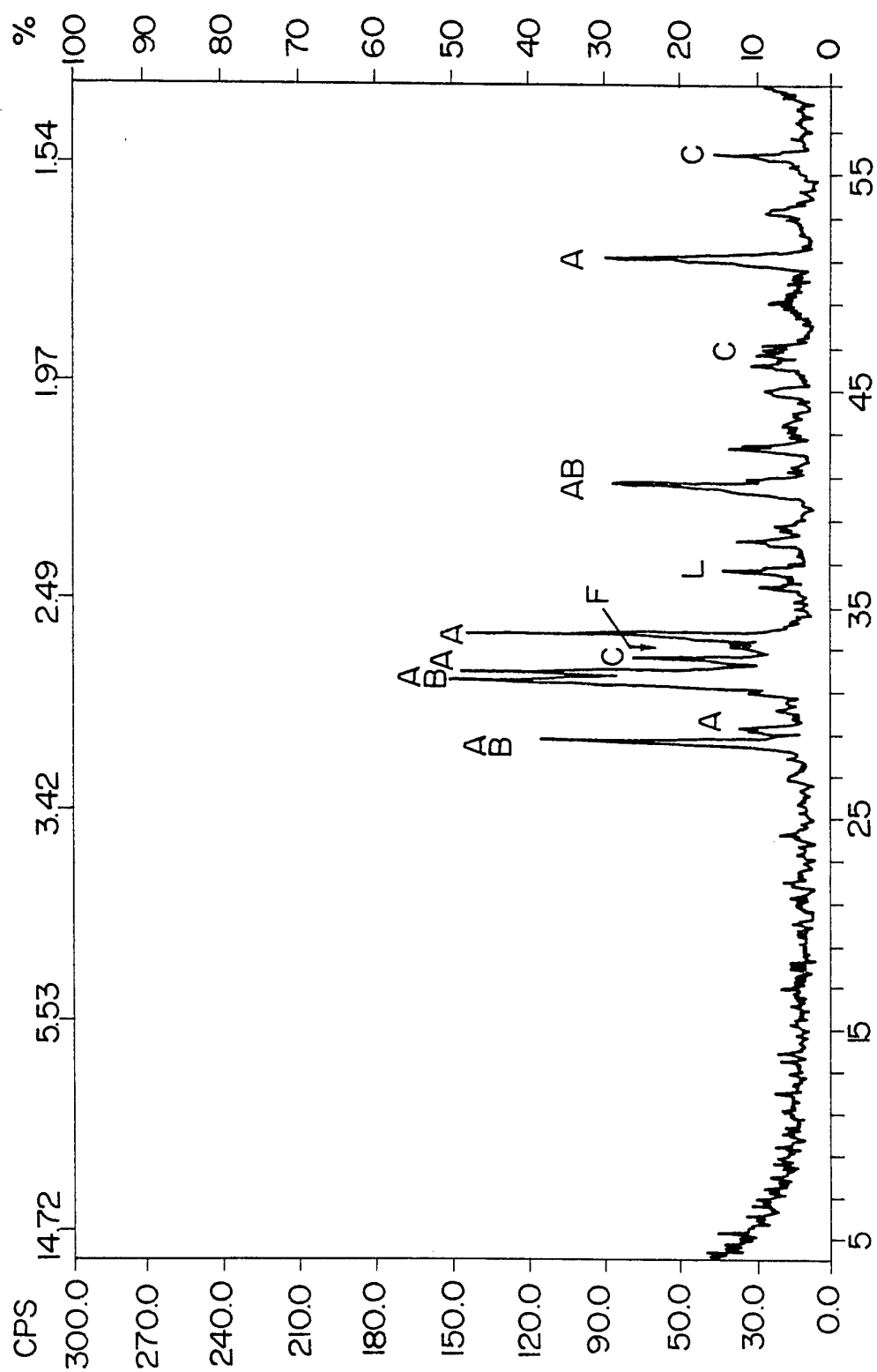
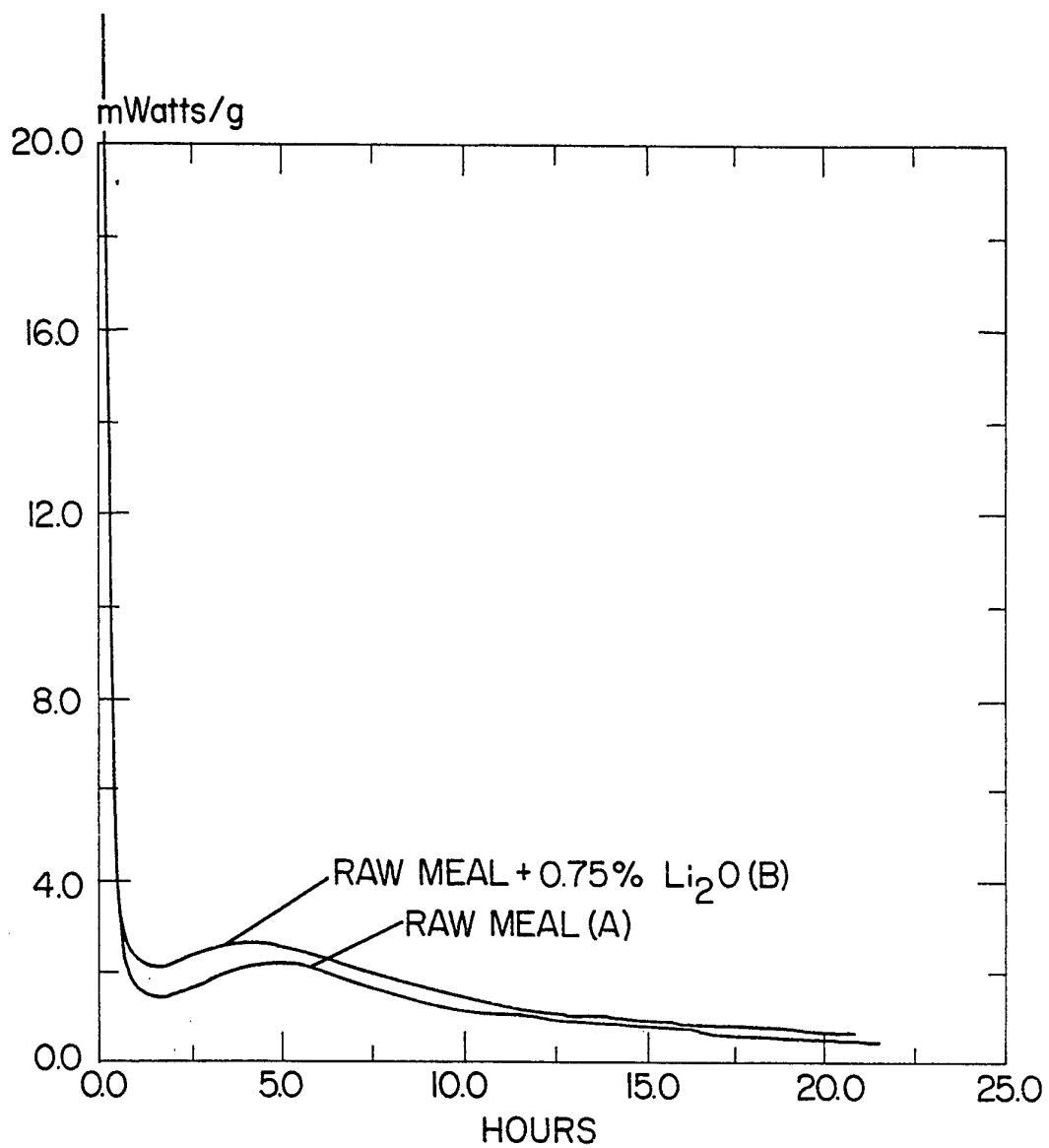


FIG. 1.

2/3

FIG. 2.

3/3

FIG. 3.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/14346

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B7/60 C04B7/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 125, no. 20, 11 November 1996 Columbus, Ohio, US; abstract no. 255289, J.GAJDA: "Development of a lithium bearing cement to inhibit alkali-silica reactivity in hardened concrete" XP002022911 see abstract & WORLD CEM., vol. 27, no. 8, pages 58-74, --- -/--	1,2



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 January 1997

Date of mailing of the international search report

23.01.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Theodoridou, E

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 96/14346

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 82, no. 12, 24 March 1975 Columbus, Ohio, US; abstract no. 76519q, O.KORAB ET AL.: XP002022912 see abstract & ZB. PR. CHEMICKOTECHNOL. FAK., - 1974 pages 301-306, ---	1,6,7, 11,13, 16,17,19
A	CHEMICAL ABSTRACTS, vol. 121, no. 2, 11 July 1994 Columbus, Ohio, US; abstract no. 16366, S.DIAMOND ET AL.: "The mechanisms of lithium effects on ASR" XP002022913 see abstract & 9TH INTERNATIONAL CONFERENCE, ALKALI-AGGREGATE REACTION IN CONCRETE, SLOUGH, UK, vol. 1, pages 269-278, ---	1
A	CHEMICAL ABSTRACTS, vol. 121, no. 2, 11 July 1994 Columbus, Ohio, US; abstract no. 16251, I.JAWED: "Alkali-silica reactivity- a highway perspective" XP002022914 see abstract & 9TH INTERNATIONAL CONFERENCE ALKALI-AGGREGATE REACTION IN CONCRETE, SLOUGH, UK, vol. 1, pages 471-476, ---	1
A	DATABASE WPI Section Ch, Week 7623 Derwent Publications Ltd., London, GB; Class F09, AN 76-42642X XP002022915 & JP 51 045 698 A (AGENCY OF IND SCI TECH) , 20 April 1976 see abstract -----	1