Studies on Inorganic Plastic Materials
Cold Molding, Setting and Hardening

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Some of R_2O_3, RO_2 and RO type metallic oxides, or limestone and clay, can be burnt to form silicates and aluminates, the reaction of which with water leads to the setting and hardening of the Portland cement. Some burnt materials containing the component R_2O_3, RO_2 or $R_2O_3 \cdot RO_2$ type metallic oxides are ready to set with lime and water. Such mortars and cements as pozzolana-lime, slag-lime, burnt clay-lime, burnt shale-lime and coal ash-lime are made for this purpose. The masonry cement, which gives more plastic mortar than ordinary Portland cement is produced by finely grinding a mixture of Portland cement and slag-lime or pozzolana-lime. The unburned sand-lime mortar has been used in some places too. All that mentioned above are casting air set plastic materials.

The well known sand-lime brick (1) and shale-lime Rostone (2) are made by stiff mud molding process with steam (about 120 psig) hardening. As steam hardening process is considered to be expensive at here, water hardening after air setting would be better. Water hardening red mud-lime brick was tried to make (3), but lime is still expensive, as compare with the low price of burnt clay brick in Taiwan.

We tried to find whether the mixes of R_2O_3, RO_2, $R_2O_3 \cdot RO_2$ and RO type metallic oxides, or the substances containing such oxides which are grinded more finely and molded under higher pressure than usual, can be air set and water hardening to give some nice articles for special use. As the first work, a comparision of the cold molding air hardening and water hardening of some plastic materials, in respect of the strength, dry and wet strength, the oxide-lime ratio, and the ferric oxide addition was worked out.

EXPERIMENTAL WORK

Materials

Portland cement, white cement, masonry cement, pozzolana, coal ash, red mud, shale, bauxite, kaoline, clay, alumina, ferric oxide, titanium dioxide and hydrated lime were used. Except shale and kaoline, all materials are domestic products. They were dried, grinded and screened through a 200-mesh screen before use.

Test Specimen Molding

300 g of oxides-hydrated lime mixture and 24—25 g of water are mixed throughlv in a mixer to form stiff mud. One gram of stiff mud was molded in a steel mold, under a pressure of about 80 kg/cm^2 or 1120 psig. The specimens rae flat sheets with a length of 2 cm, a width of 1 cm and a thickness of 0.24—0.25 cm. One hundred and eighty pieces are made for one experiment of each material.

Bending Test

For taking the mean value of bending force p in kg, two pieces of the same specimen were used in each test. Substituting b=1cm,h= 0.25cm, l=1cm in $\sigma=\frac{6\ \mathrm{pl}}{4\ \mathrm{bh}^2}$, gives $\sigma=24$p, the bending stress in kg/cm^2. Usually after first set in air, then let the specimen harden in atomospheric air, saturated moisture or clear water. During the hardening was proceeding, bending test was measured at their original states every other day. Ifthe

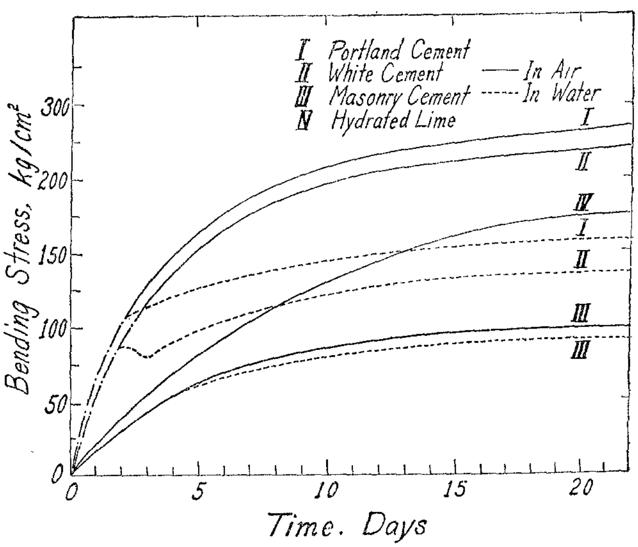

Fig. 1 Hardening of Porrland Cement, White Cement, Masonry Cement and Hydrated Lime

bending stress is plotted as ordinate vs. the aged time as abscissa, the diagrams of Portland cement, white cement, masonry cement and hydrated lime are given in Fig. 1.

Bending sress vs. aged time plots of kaoline—lime, pozzolana—lime, red mud—lime, clay—lime and sand—lime are shown in Fig. 2

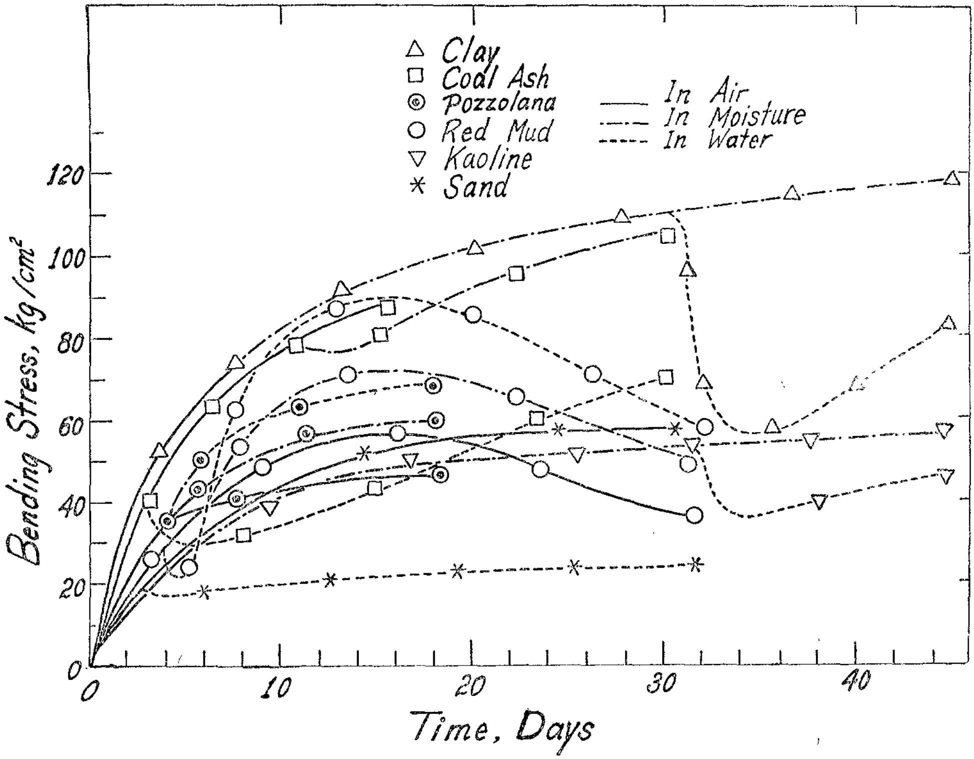

Fig. 2 Hardening of Kaoline—Lime, Coal Ash—Lime, Pozzolana—Lime, Red Mud—Lime, Clay-Lime and Sand-Lime

Fig. 3 Shows the plots of bauxite—lime, ferric oxide—lime, titanium dioxide—lime; alumia—lime and shale—lime.

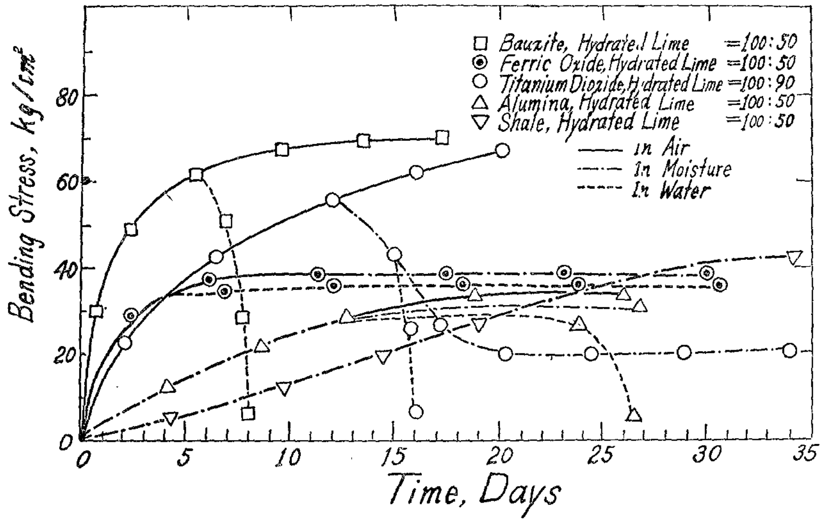

Fig. 3 Hardening of Bauxite—Lime, Ferric Oxide—Lime, Titanium Dioxide—Lime and Shale—Lime

Oxides-Lime Ratio

Three different oxides-lime ratios were used in alumina-lime, clay-lime and kaoline-lime oxides mixes, Fig. 4 shows the resulting water hardening strength.

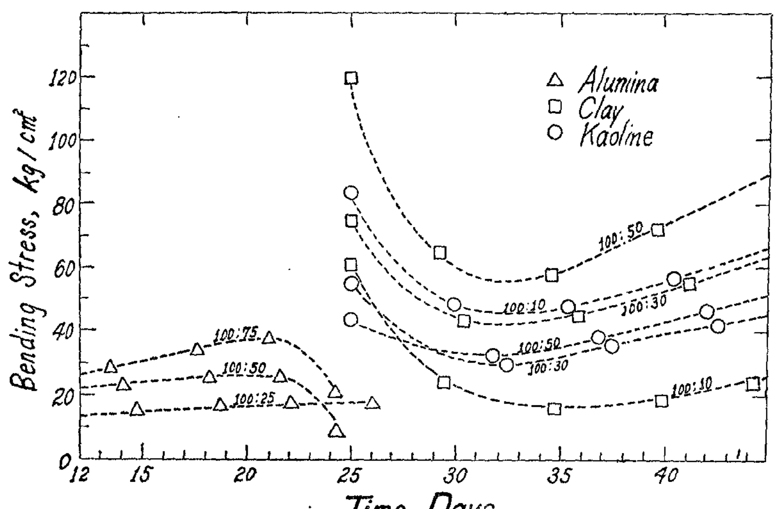

Fig. 4 Hardening of Alumina—Lime, Clay—Lime, and Kaoline—Lime at Various Oxides—Lime Ratio

When several different ratios of pozzolana-lime, red mud-lime and coal ash-lime were used, as is show in Fig. 5, the resulting water hardening strength is proportional to the oxides-lime ratio.

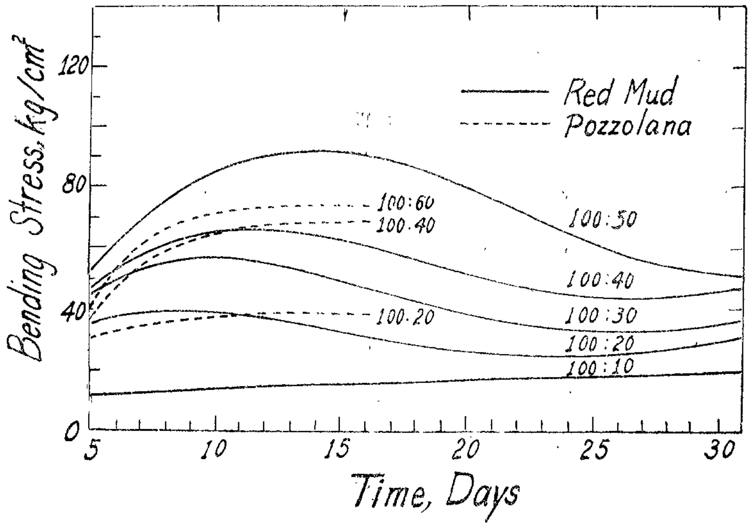

Fig. 5 Hardening of Pozzolana Red Mud at Various Oxides—Lime Ratio

In case of coal ash, the plot of 100:20 Lime ratio by weight gives the highest value, as show in Fig. 6.

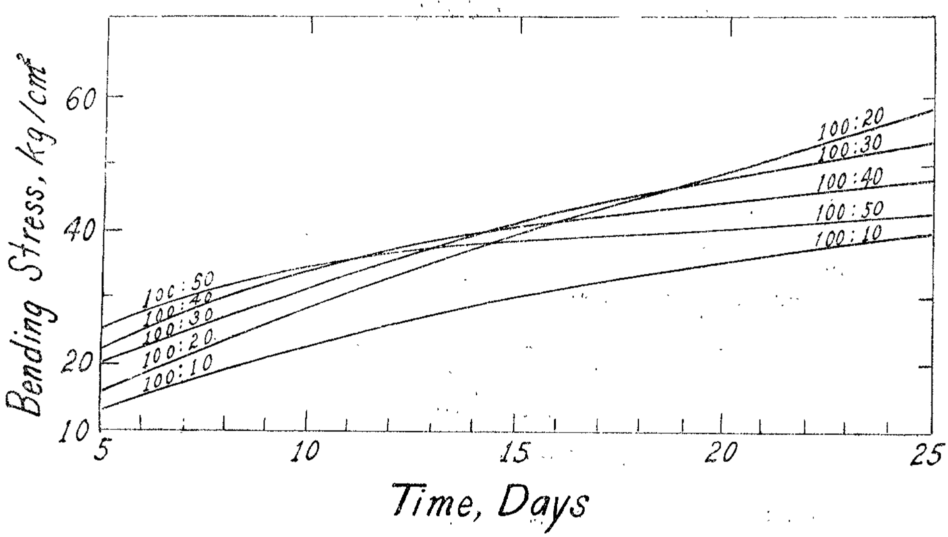

Fig 6 Hardening of Coal Ash at Various Oxides—Lime Ratio

Dry and Wet Strength

The dry and wet bending stress of red mud-lime, pozzolana-lime and coal ash-lime are shown in Table I and Fig. 7.

Table I. Bending Test in Original and Dried States

Material	Oxide-Lime Ratio	Hardening Process	Aged Time Days	Bending Stress, kg/cm² Original	Dried	$\triangle\sigma$ Kg/cm²
Pozzolana	100:40	Air	16	48	65	17
〃	〃	Moisture	16	58	58	0
〃	〃	Water	16	69	55	—14
Red Mud	100:50	Air	25	46	58	12
〃	〃	Moisture	25	67	94	27
〃	〃	Water	25	60	106	46
Coal Ash	100:50	Moisture	25	108	168	60
〃	〃	Water	25	43	84	41

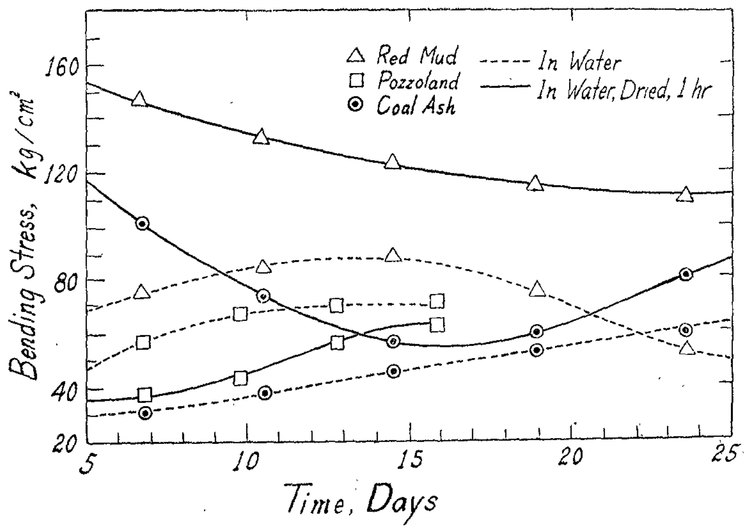

Fig. 7 Influence of Water Content on Bending Stress

A comparison of the dry strength of pozzolana, coal ash and red mud with some commercial products is shown in Table II.

Table II. Bending Stress of Oxide Mixes and Commercial Products

Oxide Mixes	Aged Time Days	Dry Bending Stress Kg/cm^2
Pozzolana-Lime	20	107—120
Coal Ash-Lime	25	84—120
Red Mud-Lime	25	103—113
Cement Slate	Years	183—190
Burnt Clay Brick	Years	45—60

Mixed Oxides Containing Ferric Oxide

Two mixed oxides are made for experiment: (1) Al_2O_3 20, SiO_2 10, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ 50, Fe_2O_3 20, Ca $(OH)_2$ 50 and (2) Al_2O_3 40, SiO_2 20, Fe_2O_3 40 $Ca(OH)_2$ 50. The effect of the ferric oxide on the strength of mixed oxides are shown in Fig. 8.

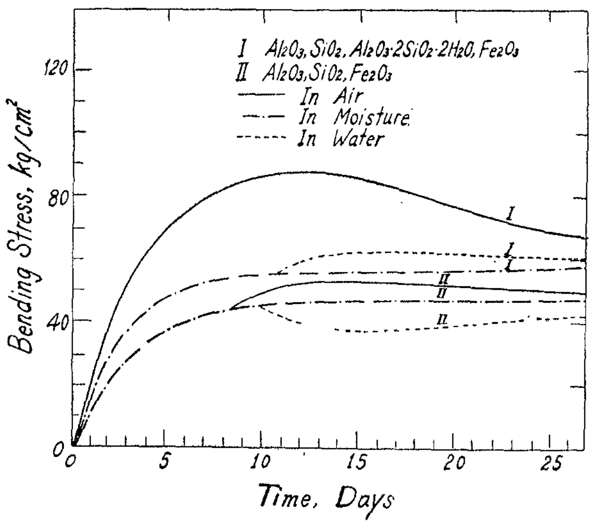

Fig. 8 Influence of Ferric Oxide on Hardening Strength

DISCUSSION OF RESULTS

For concrete, three kinds of strength test has been used, that are the tensile test, the compression test and the bending test. But for the cold molding articles which are usually of smaller size or thinner sheets than casting ones, only the bending test was adapted here. We want to know the hardening strength of various materials in the states where they will be set up to use. Bending stress of specimenes were measured, therefore, at the original states where they were undergoing various hardening process.

As shown in Fig. I, both Portland cement and white cement air hardening specimens, aged 20 days, gave a high bending stress of 220 kg/cm^2. Those of water hardening specimens were less than 150 kg/cm^2. Hydrated lime had an air hardening value of less than 175 kg/cm^2. Masonry cement had merely the value of about 80 kg/cm^2 in both water hardening and air hardening processes. As it is true in most cases, the masonry cement, a mixture of lime and Portland cement, that have components of opposite hardening properties, gave a strength less than that of its components, and showed a small strength difference between the air and water hardenings.

Red mud-lime, after 12 days air set, gave a maximum value of water hardening strength and decreased suddenly (Fig. 2). In the case of pozzolana—lime and coal ash—lime, that the plots showed a low value at the first few days and increased fast after 20 days set, represent a high water hardening propertyt.

Sand-lime showed the lowest value among all the curves, and did no increase much. Both clay and kaoline were broken in water, even after 10 days set. Fig. 2 shows the plots that was hardening after 30 days set. Although the value fell down very much in the first day of water treatment, rose gradually as hardening was proceeding. Clay was much better than kaoline (the pure clay) when used for this purpose.

In Fig. 3 the curves of bauxite and alumina show that they were not water hardening. As ferric oxide—lime gave almost a constant bending stress value of 40 kg/cm² in both air and water harhening, it can be considered to be a fast water hardening oxides mixture. The moisture hardending of shale—lime had a value as high as kaoline.

The results mentioned above may be summarized as follows:

Table III The Hardening of Various Materials:

Materials	Water Hardening	Air Hardening	Air and Water Hardening
Portland Cement	+++		
White Cement	+++		
Masonry Cement	++		
Pozzolana-Lime	++		
Coal Ash-Lime	+		
Red Mud-Lime	+		
Sand-Lime	+		
Ferric Oxide-Lime	+		
Clay-Lime			+
Kaoline-Lime			+
Hydrated-Lime		++	
Alumina-Lime		+	
Titanium-Lime		+	
Shale-Lime		+	
Bauxite-Lime		+	

Lime Ratio and Hardening

From the bending stress vs. aged time plot (Fig. 1) ane the carbonation of hydrated lime, it is not difficult to realize that the strength caused by air hardening is proportional to the lime ratio. As no evidence was needed for the air hardening experimant. only that concerning water hardening was worked out for various materials at different lime ratio. As is shown in Fig. 4, alumina-lime are air hardening, for as the lime ratio increased, the water hardening property decreased. Clay and kaoline after 25 days air set, gave values that were proportional to the lime ratio. They decreased suddenly in water but still kept the same relationship after passing the minimum points of the curves.

As the water hardening strength of red mud rose with the lime ratio, the 100:50 one showed the maximun strength at 15 days and approached a constant value with other lines in one month (Fig. 5). The plot of pozzolana showed the same relation as red mud. But in the plots of coal ash in Fig. 6, one of 100:20 lime ratio gave the highest value of all. All these three are the same water hardening materials, but the effect of lime ratio on their hardening strength are different.

Water Content and Bending Stress

The higher the water hardening, the less are the differences between dry and wet strength and between various hardening process. As shown in Table I, coal ash would be more water hardening than red mud for this reason. For the dry and wet strength of pozzolana-lime gave the same value in case of moisture hardening, it was found from its bending stress vs. aged time diagram that the wet strength in the water hardening process decrased after dry and approached a constant value. Anything that has a higher strength in wet state than it is dried, will be considered to have a good affinity with water and is water hardening.

Ferric Oxide and Water Hardening

As is shown in Fig. 3 ferric oxide gave nearly a constant bending stress of 30 kg.cm^2 at 5 days after setting. That is its water hardening property is rather faster than others. If it is true, better strength would be obtained, when ferric oxide is mixed with other not water hardening materials. The plots of the two mixes, (1) Al_2O_3, SiO_2, $Al_2O_3 \cdot SiO_2$, Fe_2O_3, (2) Al_2O_3, SiO_2, Fe_2O_3 in Fig. 8 showed that in the presence of ferric oxide these two mixes gave a quicker water hardening after 10 days air setting, as compare with those of its components Al_2O_3, SiO_2, or $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, which would be broken at that time or could only stayed in water after one month air setting.

SUMMARY

In the cold molding, setting and hardening of inorganic plastic materials such as pozzolana, red mud, coal ash, clay, bauxite, shale, alumina, sand, ferric oxide and titanium dioxide, we found:

1. Pozzolana—lime, coal ash—lime, red mud—lime and ferric oxide—lime are more water hardening, shale—lime and sand—lime are less water hardening, while alumina—lime, clay—lime and titanium dioxide—lime are not water water hardening.
2. The hardening of those that are not water hardening, are due to the air hardening of hydrated lime by carbonation.
3. The hardening of those water hardening materials are due to the hydration of silicates formed during molding and first setting.
4. Oxides-lime ratio has different effect in eifferent materialis, Only in case of weak water hardening oxides, the higher ratio gives the higher strength.
5. The more the water hardening property of the materials the less is the difference between the dry and wet bending stress.
6. Addition of ferric oxide to the less or not water hardening materials such as clay, alumina and silica, improves the water hardening very much and let them can be set in water for water hardening early.
7. Some oxides mixture gives a dry bending stress of 137 kg/cm^2, as high as two to four times the bending stress of burnt clay brick and Portland cement—sand (1:1) mortar.

LITERATURE CITED

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關於無機可塑物質之研究 其一
壓形安放及硬化處理

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火山灰、煤灰、紅泥、陶土、粘土、礬土、頁岩、氧化鋁、矽砂、氧化鐵及氧化鈦等無機可塑物質之硬化實驗結果如下：

一、火山灰石灰，煤灰石灰，紅泥石灰和氧化鐵石灰水硬性強；頁岩石灰和矽砂石灰水硬性弱而氧化鋁石灰，粘土石灰和氧化鈦石灰非水硬性。

二、非水硬性物質之硬化係由於消石灰之碳酸化。

三、水硬性物質之硬化係由於在壓形安放中所生成的矽酸鹽等之水和作用。

四、石灰含量比對不同物質有不同效果。弱水硬性物質之強度與石灰比成正比。

五、水硬性愈大者，其乾濕強度差亦愈小。

六、加氧化鐵於非水硬性物質，可增加其耐水性而可浸水。

七、有些物質其乾時抗折力甚高，約爲紅磚，水泥砂漿等之三、四倍。