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Assessment of Key Properties of Solidified Fly Ash with and without Sodium Sulfate

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ABSTRACT

The adoption of the United States Environmental Protection Agency's Coal Combustion Residuals (CCR) regulations has stirred renewed interest in the stabilization/solidification (S/S) of fly ash residuals stored in landfills and surface impoundments. Soil mixing methods can be used to S/S a variety of materials to improve static slope stability, resistance to dynamic and static liquefaction, geotechnical properties for handling and movement, and to provide a stable surface upon which to construct a final cover for closure in place or to repurpose the site for other uses. While many geotechnical studies of fly ash reuse as a construction material have been conducted, studies of *in situ* S/S (ISS) of fly ash are limited. Further, most of the work to date has involved mixing lime or Portland cement with fly ash. While these conventional approaches can be successful, limited research has shown the potential for improved performance through the addition of sodium sulfate salt during mixing of fly ash with cement. The need for additional study of fly ash ISS is a direct result of the recently passed CCR regulations. In order to assess the feasibility of ISS, a study was designed and conducted to examine the use of ISS with lime and Portland cement to improve the ash properties in addition to assessing the potential benefits in ash improvement associated with using sodium sulfate salt in conjunction with Portland cement. Performance measures included unconfined compressive strength (UCS) and hydraulic conductivity. The results indicate that improved geotechnical performance can be achieved when sodium sulfate salt is a component of a cement based mix design for the ISS of fly ash using soil mixing methods.

INTRODUCTION

According to the United States Environmental Protection Agency (EPA 2016), over 800 million tons of coal was processed in 2012 at approximately 470 coal-fired electric power plants located throughout 47 states and Puerto Rico which generated approximately 110 million tons of Coal Combustion Residuals (CCRs). Also in 2012, just 40% of this material was beneficially reused, with the remaining 60% being placed in surface landfills and impoundments. For this reason, CCRs have been historically and are expected to remain, year to year, one of the largest industrial waste streams in the United States (US). In addition to the CCRs currently being generated, there are legacy facilities and impoundments with millions of tons of CCRs all over the US and abroad.

CCRs are byproducts of coal-fired electric power plants and are made up generally of fly ash, bottom ash, boiler slag, and flue gas desulfurization material. Some of these products have been recycled to produce road base materials, manufactured aggregates, flowable fills, structural fills, and materials in the production of Portland cement for years. According to the American Coal Ash Association, (ACAA 2015), the largest volume of CCRs recycled annually is in fly ash used in concretes. The use of fly ash as a pozzolanic additive in concretes has been well studied and is widely applied in practice. Even with extensive reuse, a large amount of fly ash is still disposed in landfills and impoundments due to the fact that the supply is much larger than the demand. In addition to the excess being produced, there exists a great amount of fly ash that was generated in the past.

There are a few options available to facilities looking to close historic impoundments or to find ways to improve existing facilities for future use and compliance with the new CCR rules. One of those options is *in situ* improvement of fly ash and other CCRs through reagent addition via soil mixing. Soil mixing can be performed in a number of ways including the dry method where high moisture materials are mixed *in situ* with dry cementitious materials to improve the material properties. Soil mixing provides many benefits for ash handling including reagent addition *in situ*, i.e. limited handling; the ability to treat discrete vertical and horizontal zones; consistent horizontal and vertical reagent distribution within the mass; and, in many cases, reduced cost and schedule. Soil mixing is already widely applied for the treatment and S/S of many different, often difficult to handle, waste types and the associated impacted soils and groundwater, including, but not limited to, manufactured gas plant (MGP) tars, wood treating products, e.g. creosote, semi volatile and volatile organic compounds (SVOCs and VOCs), and chlorinated solvents. The reagent blends used to remediate these various waste types vary by industry, application, location, and site and are often designed on a case-by-case basis to meet specific property enhancement goals in unique ground conditions. Although the novel application of soil mixing for the *in situ* treatment of wastes, e.g. for implementation of *in situ* chemical oxidation (ISCO) or *in situ* chemical reduction (ISCR), has become more common over the last decade, the largest use of soil mixing for environmental remediation remains ISS with Portland cement. Despite the widespread use of soil mixing for accomplishing geoenvironmental and geotechnical improvement objectives in numerous industries, the application of soil mixing to CCR has been historically limited.

Significant research has proven the effectiveness of fly ash as a beneficial additive in concrete mixtures, so it's reasonable to expect, and has been shown in studies (Ghosh 1976, Zhang et al. 2000) that the addition of cement to fly ash will result in a mixture with improved properties relative to the fly ash alone. In addition, lime and Portland cement are frequently used in practice to improve the properties, specifically strength, of high moisture content soils. Research has also shown that an alkali activator, such as Na_2O, can have a positive effect on the compressive strength and microstructural characteristics of fly ash (Guo et al 2010) with a specific study (Ramesh et al. 1999) showing sodium salts improving the strength of fly ash-lime mixtures. According to that previous study, a very small amount of lime, when added with a sodium salt, is all that is needed to solidify the fly ash. Finally, the improved hydration of a cement formulation containing very high volumes of coal fly ash (~80% by dry mass) activated by sodium sulfate (Na_2SO_4) has been demonstrated (Donatello et al. 2013). The Donatello study found that sodium sulfate acts as a source of alkali to activate the fly ash. Comparing the performance of the sodium sulfate activated fly ash to a reference paste with gypsum instead of sodium sulfate revealed that the sodium sulfate activated material had reduced setting times, a shortened hydration period, increased early hydration, and faster compressive strength development.

Based on the above, the current study was developed and conducted to assess the improvement potential of using lime (alone), Portland cement (alone), and a combination of Portland cement and sodium sulfate salt to improve the properties of saturated fly ash. Furthermore, the study was developed in an attempt to mimic the addition of these reagent materials via a soil mixing construction approach, specifically soil mixing with dry reagent addition. The primary goal was to improve the geotechnical properties of the loose, saturated CCRs obtained from a legacy impoundment. The study was focused on increasing the strength and stiffness of the CCR material in order to provide increased bearing capacity and reduced settlement to accommodate future site use.

Although the terms stabilization and solidification are often used synonymously and simultaneously, the two terms actually describe distinct processes. According to the USEPA and in the context of environmental remediation, the term stabilization refers to processes that rely on a chemical reaction to make contaminants less leachable whereas solidification refers to binding processes that physically encapsulate or block contaminants from moving. In many situations, both processes are contributing to the overall reduced contaminant mobility, but there are cases when one or the other is completely controlling. In a broader sense, specifically in the context of geotechnical engineering, the term solidification can be used to describe processes that turn a liquid or semi-liquid into a solid or semi-solid. Given the goals of this study, i.e. primarily geotechnical improvement, the term solidification will be used to describe the property improvement process throughout this paper.

EXPERIMENTAL MATERIALS AND METHODS

Materials: The CCR used in this study was obtained from the site of a former wet-ash handling storage lagoon. The samples were auger cuttings from a geotechnical investigation through the retired ash lagoon. Geotechnical index properties of the CCRs used in this study can be found in Table 1. As shown in Table 1, 7 different CCR samples were subjected to physical property testing. Water content was measured by drying the material for 24 hours at 105 ^{o}C (ASTM D2216-10). Dry density was determined for a simulated hydraulic disposal condition by first filling a graduated cylinder with water, adding dry fly ash to sediment through the water, and measuring the volume of sedimented ash. This procedure would produce the lower limit of dry density. The particle density, or specific gravity, was measured for only sample 1 using ASTM D854-14.

Table 1. Fly Ash Properties from Laboratory Testing

Sample	Water Content, *w*	Specific Gravity, S.G.	Dry Density, ρ_d
	(%)	-	(g/cm^3)
1	26	2.41	1.22
2	41	-	1.17
3	23	-	1.28
4	23	-	1.32
5	27	-	1.25
6	24	-	1.25
7	27	-	1.23
Average	28	2.41	1.25

A number of other commonly presented geotechnical index properties, calculated from the properties in Table 1, are presented in Table 2.

Table 2. Fly Ash Properties Calculated from Laboratory Testing Results

Sample	Porosity, n	Degree of Saturation, S	Saturated Density, ρ_{sat}	Saturated Water Content, w_{sat}
	-	(%)	(g/cm^3)	(%)
1	0.49	65	1.71	41
2	0.51	94	1.69	44
3	0.47	64	1.75	37
4	0.45	68	1.77	34
5	0.48	69	1.73	39
6	0.48	63	1.73	38
7	0.49	69	1.72	40
Average	0.48	70	1.73	39

The properties presented in Table 2 would be representative of the subject fly ash in its loosest state.

In order to confirm the average saturated water content of 39%, calculated using the measured specific gravity of 2.41, the saturated water content of the composite mixture was also measured by sedimentation of fly ash in a graduated cylinder. Using mass and volume measurements, the measured saturated moisture content, 39%, matched exactly with the calculated saturated moisture content expected for the composite mixture.

Based on the similarity of the engineering properties across all seven samples and because of a limited supply of individual samples, the seven samples were mixed together to produce a composite sample for further testing.

The gravimetric water content of the composite sample, measured immediately prior to mixing, 23.6%, was lower than the expected average moisture content of 28% shown in Table 1 and also lower than the expected saturated moisture content of the composite. The difference between the measured and expected moisture content is attributed to moisture loss during sample storage and mixing.

Building upon the previous studies described in the background section and as noted above, this study was undertaken to determine if cement or lime and fly ash mixtures, i.e. conventional *in situ* mixing formulations, can be improved through the addition of sodium sulfate salt. The components, saturated fly ash, lime, cement, and sodium sulfate salt, as a % of dry fly ash mass, used to create the 14 mixtures tested in this study are summarized in Table 3. Unfortunately, due to time constraints, no mixes of lime and sodium sulfate were created or tested in this study.

Table 3. Summary of Mixture Components (%'s of Dry Ash Mass)

Sample ID	Pore Water[1]	Added Water[2]	Lime	Portland Cement	Sodium Sulfate Salt
1	23.6	15.6	0	1.5	0
2			0	3.0	0

3			0	4.5	0
4			0	6.0	0
5			1.5	0	0
6			3.0	0	0
7			4.5	0	0
8			6.0	0	0
9			0	4.5	2.0
10			0	4.5	4.0
11			0	4.5	6.0
12			0	6.0	2.0
13			0	6.0	4.0
14			0	6.0	6.0

[1]Pore water calculated from measured moisture content of 23.6%
[2]Added water = tap water added to bring moisture content up to saturated moisture content

Methods: In order to mimic saturated conditions, the water content of the composite was adjusted up to the saturated water content, 39%, through the addition of tap water, prior to mixing with the reagents.

After moisture conditioning, the reagent additives were mixed with the ash in the proportions shown in Table 3. Since previous research discussed earlier demonstrated possible benefits of sodium sulfate salt in conjunction with Portland Cement, the experimental program only used the salt with mixtures containing Portland Cement. Reagent addition and mixing was generally performed according to the following procedure, add the fly ash and water to the mixing pan, mix the fly ash and water until visually homogeneous, add lime or cement, mix the saturated fly ash with the solidification reagent until visually homogeneous, add dry salt (if included), and mix until visually homogeneous. At all steps, mixing was completed by hand until no large unmixed lumps were noticeable by passage of a steel spoon across the bottom of the mixing pan. Once mixing was complete, the mixtures were added to plastic cylinders having dimensions of 71mm diameter and 142 mm in length. Samples were initially cured for one-day and then submerged in water for the remainder of the curing period prior to removal for testing.

RESULTS

Cured samples were subjected to unconfined compression (ASTM D2166) and permeability (ASTM 5084) testing to determine the unconfined compressive strength (UCS) and hydraulic conductivity, respectively. The results of the testing performed in this study are summarized in Table 4. Time available for this student limited the number of hydraulic conductivity tests.

Table 4. Unconfined Compressive Strength and Hydraulic Conductivity Results

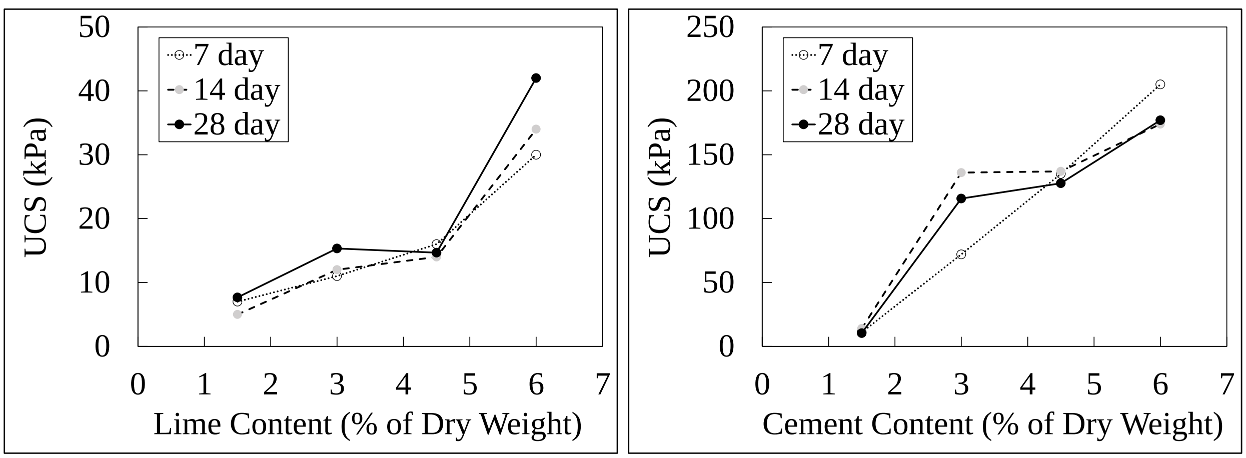
	Unconfined Compressive Strength (kPa)					Hydraulic Conductivity (cm/s)
Sample ID	7 day	14 day	28 day 1	28 day 2	28 day 3	28 day
1	11	14	12	11	8	

2	72	136	83	140	124	
3	135	137	119	108	156	2.7x10^{-6}
4	205	174	214	143	174	2.5x10^{-6}
5	7	5	9	9	5	
6	11	12	16	13	17	
7	16	14	12	16	16	
8	30	34	36	42	48	
9	214	268	272[1]	247[1]	128[2]	
10	124	219[2]	268[1]	159[2]	-	
11	207	405[2]	338[2]	267	262[1]	
12	215	544[2]	351[2]	689[1]	602[2]	
13	375	631	415	445[1]	283[2]	
14	557[2]	600[1]	697[1]	697[1]	608[1]	3.3x10^{-6}

Note: [1]Result indicates the vertical failure planes were indicative of a tensile rather than shear failure and thus not rpresentative of the shear strength of the sample [2]Result indicates the failure plane was indicative of a definite premature break

A more detailed discussion about the potential causes of a premature break and statistic variability of UCS testing in general is provided below in the discussions. Unfortunately, due to time constraints, hydraulic conductivity testing was limited to a small subset of the mixtures and no mixes containing lime were subjected to hydraulic conductivity testing.

Figure 1a shows the UCS of the solidified fly ash mixtures vs. lime content and Fig. 1b shows the UCS of the solidified fly ash mixtures vs. cement content.

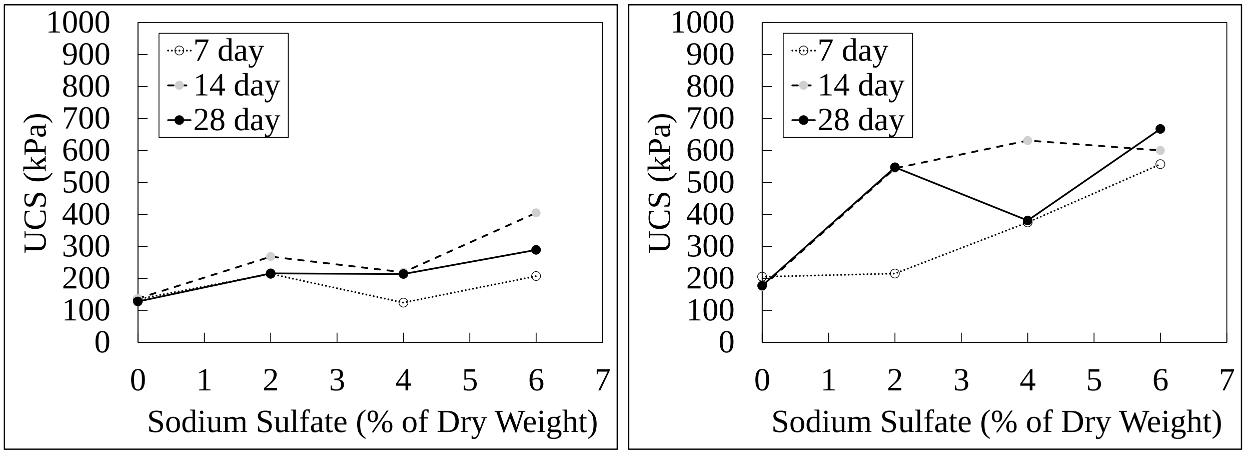


(a) (b)

Figure 1a. UCS of solidified fly ash vs. lime content and 1b. UCS of solidified fly ash vs. cement content

Note, the scale of Fig. 1a is different than Fig. 1b to allow the reader an opportunity to review the information in Fig 1a. Using a similar scale for both figures would have rendered the information in Fig. 1a difficult to review.

Figure 2a shows the UCS as a function of sodium sulfate salt content for solidified mixtures including Portland cement at a rate of 4.5% and Fig. 2b shows UCS as a function of sodium sulfate content for solidified mixtures including Portland cement at a rate of 6%.



(a) (b)

Figure 2a. UCS of solidified fly ash (4.5% Portland cement) vs. sodium sulfate content and 2b. UCS of solidified fly ash (6% Portland cement) vs. sodium sulfate content

DISCUSSION OF RESULTS

General: Throughout the data set there are data points that are inconsistent with the trends indicated by the remainder of the data and with expectations from experience with similar materials and studies (e.g. strength increases with curing time and strength increases with increasing cementitious material content). The authors attribute at least some of these outliers to premature brittle failures from unconfined compression testing on imperfect samples. Testing of imperfect samples can result in stress concentration and premature tensile failures during the test. Figure 3 includes two photographs of samples tested in this study, one with a typical shear plane and one with vertical tensile cracks indicative of a tensile failure.

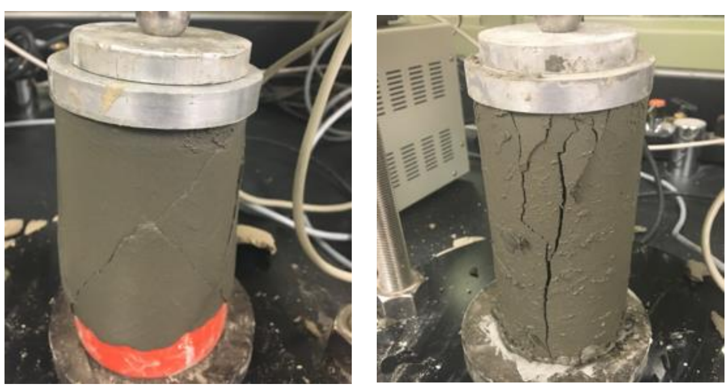


Figure 3. Unconfined compressive strength test samples with shear (left) and tensile (right) failure

As shown on Table 4, triplicate tests were conducted on theoretically "identical" specimens after the samples had cured 28 days. For data presentations in Figs. 1 and 2, these additional data points were averaged. However, a review of the individual data sets is important in the context of explaining the outlier results discussed above. As one familiar with testing solidified materials would expect, the replicate tests showed substantial variability specimen to specimen. One way to look at this variability is to compare the minimum and maximum observed values to the average value, i.e. percent difference. Another way to look at the variability that is common in the soil mixing industry is to calculate the coefficient of variability which is simply the ratio of the standard deviation to the mean. A summary of observed variability, as represented by these metrics, for the 28 day sample set is presented on Table 5.

Table 5. Variability Metrics for 28 Day Strength Data

	Overall Average Variability	Greatest Observed Variability
Min (below average)	23%	40%
Max (above average)	18%	26%
Coefficient of Variability	0.18	0.29

The observed variability from this study is well within expectations when compared to the industry "rule of thumb" for UCS which is generally +/- 50% of the mean and published ranges of coefficients of variability for soil mixed material being in the range of 0.3 to 0.7 with an average around 0.5 (Bruce 2000). The lower coefficients of variability observed in this study are also consistent with expected lower variation in properties in laboratory studies where more control is exercised over the reagent addition and mixing processes as compared to field mixed samples. The authors crafted the remaining discussions to provide some useful consensus observations with these general observations (limitations) in mind.

Hydraulic Conductivity: Although the hydraulic conductivity data is limited, a couple of findings seem clear from a review of the data. First, cement stabilized fly ash has similar or lower hydraulic conductivity than the fly ash itself (typically in the 10^{-5} to 10^{-6} cm/s range (Kim et al., 2005)). Second, rounded to the nearest one significant figure, $k = 3x10^{-6}$ cm/s was measured in all tests indicating little benefit or penalty associated with additional cement or sodium sulfate salt.

Figure 1: A couple of general findings are apparent from a review of Fig. 1a. First, the improvement in strength with curing time is consistent with other solidified materials, i.e. generally (ignoring the results from the 4.5% lime sample set) the 28 day strength is 30% to 50% higher than the 7 day strength. Second, there appears to be a threshold lime content, somewhere between 4.5% and 6%, needed to appreciably improve the compressive strength.

Similar findings are apparent from a review of Fig. 1b. First, there is clearly an improvement in compressive strength as the Portland cement addition rate increases. As with the lime mixtures, there appears to be a threshold value, but the threshold value seems to be much lower for the Portland cement mixtures, between 1.5% and 3%. Although one would expect to see strength gain with time, the data does not indicate that any significant strength gain is taking place between 7 and 28 days. This is attributed to the premature break issues discussed above.

Figure 2: A few trends are evident from a review of Fig 2. First, there appears to be strength increase with time, at least from 7 to 14 days. Second, there appears to be an increase in strength with increases in sodium sulfate salt content. Third, the most substantial compressive strength improvement, perceivably from sodium sulfate salt addition, occurs between 0% and 2% sodium sulfate salt addition with higher additions of sodium sulfate salt, 4% and 6%, exhibiting less benefit.

Comparison of Fig. 2a to Fig. 2b indicates that there is appreciable strength improvement for a modest increase in cement content, from 4.5% to 6%. In both cases, increasing the sodium sulfate salt content beyond 2% seems to offer little benefit.

LIMITATIONS AND FUTURE STUDY RECOMMENDATIONS

The authors acknowledge that this study was limited in scope and therefore the results must be reviewed with the limitations in mind. First, due to time constraints, the final study ended up being much smaller than the planned study, which included substantially more reagent combinations, 40 vs. 14. Additional reagent combinations that could or should have been tested might have included investigation of other salts, focused evaluation of the threshold strength zones for both solidification reagent and salt addition, and salt addition to mixtures containing lime. Second, the study was ended after 28 days. Although observed strength gain past 28 days for mixes containing only Portland cement or lime is generally limited, it would have been beneficial to evaluate strength gain of these mixes at 56 and / or 112 days to confirm past findings. Finally, a more detailed analysis, including remixing and retesting, of the outlier results would also have been beneficial.

The authors also feel that additional study of fly ash solidification and / or stabilization is warranted. In addition to the suggestions made for improvement of this study, future studies should also focus on assessing additional reagents (e.g. slag), refining addition rates, confirming the benefit of salts, assessing cost effectiveness and practicality, and assessing differences in reagent mixtures relative to ash source, type, and properties. As the CCR rules trigger expanded monitoring and closure of existing facilities and impoundments, the authors expect that the study and use of soil mixing of fly ash will be greatly expanded.

SUMMARY AND CONCLUSIONS

Some of the practical implications of the above results and discussions are:

- The UCS of untreated saturated fly ash is nearly zero.
- The addition of lime to saturated fly ash in laboratory experiments designed to simulate the soil mixing dry mix method produced 28 day UCSs from 7 to 42 kPa (1 to 6 psi) as the lime content went from 1.5% to 6% on a dry mass basis.
- The addition of Portland cement to saturated fly ash in laboratory experiments designed to simulate the soil mixing dry mix method produced ultimate UCSs in the range of approximately 10 to 200 kPa (approximately 1 to 30 psi) for cement contents of 1.5% to 6% on a dry mass basis.
- The addition of sodium sulfate to mixtures including Portland cement may provide further benefit with ultimate laboratory UCSs in the range of 600 to 700 kPa (approximately 90 to 100 psi).
- Based upon the limited hydraulic conductivity of solidified fly ash appears to be lower than the typical values of hydraulic conductivity of the ash itself and is relatively insensitive to cement content and sodium sulfate addition.

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