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A NEW ACCELERATED METHOD FOR DETERMINING THE POTENTIAL ALKALI-CARBONATE REACTIVITY

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ABSTRACT

Many kinds of carbonate aggregates with different chemical compositions, structure, and geological characteristics have been investigated systematically, and the Kingston aggregate was also studied as a standard one. This research deals with chemical components and mineral analysis, petrographic examination, the dynamics of alkali-carbonate reaction with different cements, alkali contents and particle sizes. A new method for evaluating the potential alkali-carbonate reactivity has been proposed according to the results, in which the major test factors include 1.5% Na2Oeq. of alkali content, 1M NaOH solution, 0.3 water-to-cement ratio, 5-10mm particle size and 4 weeks of test period at 80°C. The results using this new method has also been compared with that of the performance of concrete structures in China.

Keywords: Alkali-carbonate reaction, Accelerated method, Reactive aggregates, Durability of concrete

INTRODUCTION

Since the field deterioration of concrete structures due to alkali-carbonate reaction (ACR) was first reported in the 50's in North America, and investigated by Swenson and Gillot (Swenson & Gillot 1957, 1964), more research attention has been paid by many researchers (Rogers 1986, Tang et al 1986). The major contents are the mechanism and test methods of ACR as well as the field inspections. The progress of ACR study leads us to know that ACR problem can not be as easily inhibited as ASR. The primary important thing is how to identify the reactive carbonate aggregates for the purpose of avoiding it. It seems that a rapid method for testing the reactivity of carbonate aggregate is essential because of the limited construction period.

A great scale of infrastructure construction has occurred in the past twenty years in China, and many limestone and dolomite aggregates have been used. The field inspection and laboratory investigation have shown that the deleterious cases have been caused by ACR in different concrete structures in several provinces in China, e.g. piles, railway ties, airports and bridges (Tong et al 1997). In all these cases high alkali cement and reactive dolomitic limestone or dolomite aggregates were used. The research works on the mechanism and test method of ACR have been continued and enhanced in recent years because of a powerful financial support by the government since 1996.

As we all know, there is no quick test method for determining the alkali reactivity of carbonate rocks in the world. The Canadian concrete method takes so longer time that it is not satisfactory for Chinese practice as mentioned by many engineers and researchers. Based on this view, a rapid method for ACR reactivity determination has previously been proposed by us (Tang et al 1994), it was based on improvement of the ASR autoclave method. It has been noted that this method poses some barriers for engineering management, e.g. too small a mortar bar size which leads a large variation of data, too small amount of aggregate which may not be the representative of actual rocks and quarries. The present project aims at developing a rapid test method for determining the alkali reactivity of carbonate rocks with a good engineering characteristics, that is more reliable and easily acceptable.

CARBONATE AGGREGATE SAMPLES

In order to obtain typical samples as much as possible, many kinds of carbonate aggregates all over China have been collected, and the quarries have also been investigated by us and the geologist at Nanjing University. The rocks tested come from different origins and geologic ages, e.g. Sinian, Cambrian, Ordovician, Dyas, Trias, etc. This almost covers all carbonate aggregates that were reported being reactive in the field concrete structures. The geologic characteristics of samples were analyzed by microscopy, and the result is shown in Table 1.

TEST METHODS

150°C Autoclave Method

This method was proposed previously by authors as a quick scanning one (Tang et al 1994). The major factors of the procedure include 150°C of test temperature, 5-10mm size of aggregates, 10% KOH of alkali solution, 1.5% Na2Oeq. of alkali content in cement and 6 hours test period. It is quite similar to " The Chinese Autoclave Method for ASR", but a different aggregate size was used.

80°C Accelerated Method

This is the purpose of the present research, in which molding and pre-curing procedures are similar to the autoclave method, but the following raw materials and test conditions were used:

- Water-to-cement ratio: 0.3, aggregate-to-cement ratio: 1:1.
- The alkali content of Standard low alkali cement from Jiangnan Cement Co is 0.52% Na2Oeq. Alkali solution KOH was added in mixing water to make 1.5% Na2Oeq of the total alkali content in cement.
- The alkali content of Standard high alkali cement from Jidong Cement Co is 1.24% Na2Oeq. Alkali solution KOH was also added in mixing water for making 1.5% Na2Oeq of the total alkali content in cement.
- Alkali storage solution: 1 M NaOH.
- Size of Specimens: 20 by 20 by 80 mm, 40 by 40 by 160 mm.
- Size of aggregates: 0.8-1.25 mm, 1.25-2.5 mm, 2.5-5 mm, 5-10 mm, The former three kinds of sizes were remarked as -1, -2, -3 following the names of rock samples.

For comparison with this method, the test was also carried out at 40°C.

TABLE 1: Carbonate Rock Samples Investigated

No	Geological age	Quarry Location	Geologic characteristics
C	Leikepo Formation, Triassic	Guanyuan, Sichuan	Macromeritic dolomite
CK	Gull River Formation, Ordovician	Kingston, Canada	Argillaceous dolomitic limestone
ZK	Triassic	Yibin, Sichuan	Dolomitic limestone
QJ	Bei An Zhuang Formation, Ordovician	Upper layer in Baofu Mountain, Lin Qu	Thin laryer structure, dolomitic limestone
LB2	Bei An Zhuang Formation, Ordovician	Lower layer in Baofu Mountain, Lin Qu	Leonard dolomitic limestone
T1	Majiagou Formation, Ordovician	Tangshan, Hebei	Dolomite
T2	Ibid.	Ibid.	Leopard dolomitic limestone
ATJ	Ibid. Standard geologic section	Ibid.	Argillaceous dolomite
T4	Majiagou Formation, Ordovician	Tangshan, Hebei	Leonard Dolomitic limestone
T5	Ibid.	Ibid.	Dolomite
JD2	Yeli Formation, Ordovician	Jidong, Hebei	Leopard deep gray limestone
JD4	Ibid.	Ibid.	Leopard light yellow limestone
Z1	Zhangxia Formation, Cambrian	Liantai Mountain, Jinan, Shandong	Leopard Oolitic limestone
Z3	Ibid.	Ibid.	Leopard Argillaceous limestone
Z5	Ibid.	Ibid.	Leopard Micritic limestone
JC1	Wu Mi Mountain Formation, Sinian	Jixian, Tianjin	Microlitic dolomite
JH1	Hongshui Mountain Formation, Sinian	Jixian county, Tianjin	Argillaceous silt dolomite
JH2	Ibid.	Ibid.	Argillaceous Microlitic dolomite
WB1	Feng Mountain Formation, Cambrian	Weifang, shandong	Argillaceous dolomitic limestone
WB3	Ibid.	Ibid.	Argillaceous limestone

All carbonate aggregates samples were crushed and graded into 5-10mm, 2.5-5mm, 1.5-2.5mm and 0.8-1.5mm for testing.

RESULTS AND DISCUSSION

ASR, ACR and Thermal Expansion by Autoclave Scanning Test

All samples were primarily tested by the quick method (150°C) for determining ASR and ACR alkali reactivity, the results are shown in Table 2. The 20 by 20 by 80 mm of mortar bar size was used in order to save the reactive carbonate aggregates. It is clear that samples JD2, JH1 and JH2 possess ASR reactivity and T5 may be potential ones. These carbonate aggregates contain much more silica components, which show more microcrystalline quartz by petrographic examination. It should be noted that these rocks appear to be alkali reactive by ACR measurement, because the expansions of mortars with these aggregates increase sharply with stored period. It can be concluded that these rocks are both alkali silica and alkali-carbonate reactive.

Besides the above rocks, the other carbonate aggregates can be identified as being non-reactive for ASR. This means that the expansions of samples caused by ASR are negligible compared with total values. On the other hand, coarse crystalline dolomite C (non ASR and ACR reactivity) or pure cement pastes or mortars shows a very low expansion at high temperature after a long treatment period. This indicates that no obvious expansion caused by heat expansion of hydration products of cement pastes and minerals in the rocks.

Influence of Particle Size on ACR Expansion

Enhance of high temperature and high alkali content and use of sensitive particle size are the theoretical base of accelerating alkali-aggregate reaction. The most important key factor of controlling AAR may be the size of aggregate particles as found by many authors. It is clear that most of methods are identified at 80°C, at which no obvious modification of the nature of hydration process, products and structures of hardened Portland cements occur. Therefore, the present research aims at a temperature of 80°C as a standard, and emphatically studies the influences of the other key factors and the expansion dynamics of various carbonate aggregates.

Various potential reactive aggregates of ACR were tested with 1.5% Na2Oeq content of cement and 1M NaOH curing solution at 80°C. The expansion of microlitic dolomite of Sinian from Tianjin with different size is shown in Fig.1. The results indicate that the expansion increases with decrease of particle size. It is reasonable that ACR and expansion is related to the surface area of reactive particles. It is noted, however, that a pessimum effect occurs usually in ACR expansion due to a complex mechanism. The samples with 5-10mm particle size show a maximum expansion, and failed by cracking at 6 weeks of age. Furthermore, the expansion curve shows a maximum slope£¨which means that this particle size is more sensitive to ACR expansion.

Fig. 2 shows the expansion curves obtained with dolomitic limestone LB from Lin Qu, Shandong province. It is also clear that the expansion increases with decreasing of particle size at an early age (up to 1 month), but a different curve appear after 1 month of age. The sample with fine aggregate demonstrates a gently period of expansion after 1 month, the others indicates a continued expansion. For the same reason, the sample with 5-10mm particles shows a largest expansion and slope.

A similar result was obtained with dolomitic limestone QJ from the same site as LB, but it is in higher level of the quarry as shown in Fig.3. The structure of QJ is similar to the international ACR reactive rock CK from Kingston, Canada. QJ shows more reactive and greater expansion than CK. These results indicate that alkali-carbonate reaction is not only related to the content of clay, but to the structure of dolomite crystals. On the other hand, the results also evidently illustrate that the sensitive particle size is 5-10mm, because the expansion with other particle size appears to stop after 5 weeks.

The expansion curve of dolomitic limestone ZK from Sichuan province is shown in Fig. 4. A similar results can be seen, but the alkali-carbonate reactivity of ZK is obviously less than that of QJ. Samples with 5-10mm particle only show a continued expansion, others indicate a gentle curve. The sensitive particle size of 5-10mm is also confirmed by this kind of carbonate rock.

TABLE 2: Expansion Behavior of Samples by Autoclave Method

No/Time	Size	ACR Expansion (%)					ASR
		6h	12h	30h	54h	80h	Test
C	5~10mm	0.029	0.040	0.038	0.060	0.056	
CK	5~10mm	0.093	0.158	0.222	0.298	0.343	0.011
LB2*	5~10mm	0.072	0.154	0.238	0.283	0.321	0.021
LB2-1	0.8~1.25mm	0.199	0.293	0.326	0.319	0.324	
LB2-2	1.25~2.5mm	0.117	0.202	0.323	0.329	0.336	
LB2-3	2.5~5mm	0.123	0.211	0.336	0.373	0.402	
QJ	5~10mm	0.099	0.190	0.321	0.406	0.481	0.021
QJ-1	0.8~1.25mm	0.127	0.182	0.249	0.241	0.246	
QJ-2	1.25~2.5mm	0.137	0.242	0.305	0.302	0.311	
QJ3	2.5~5mm	0.139	0.230	0.320			
ATJ	5~10mm	0.137	0.211	0.456	0.879		
ZK	5~10mm	0.124	0.279				
T4	5~10mm	0.117	0.224	0.404	0.496	0.591	0.066
T1	5~10mm	0.048	0.127	0.227	0.299	0.331	0.015
T2	5~10mm	0.115	0.195	0.321	0.425	0.516	0.062
T5	5~10mm	0.104	0.275	0.499	0.645	0.803	0.090
JD2	5~10mm	0.056	0.165	0.383	0.648	0.809	0.109
JD4	5~10mm	0.075	0.196	0.332	0.402	0.441	0.025
Z1	5~10mm	0.066	0.105	0.194	0.253	0.286	0.015
Z3	5~10mm	0.106	0.147	0.196	0.257	0.294	0.029
Z5	5~10mm	0.111	0.202	0.288	0.344	0.360	0.023
JC1	5~10mm	0.064	0.093	0.214	0.286	0.359	0.024
JH1	5~10mm	0.069	0.164	0.415	0.572	0.852	0.143
JH2	5~10mm	0.116	0.248	0.873			0.184
WB1	5~10mm	0.060	0.115	0.213	0.307	0.366	-0.031
WB3	5~10mm	0.076	0.130	0.237	0.299	0.434	
F2	5~10mm	0.057	0.131	0.221	0.260	0.278	-0.003

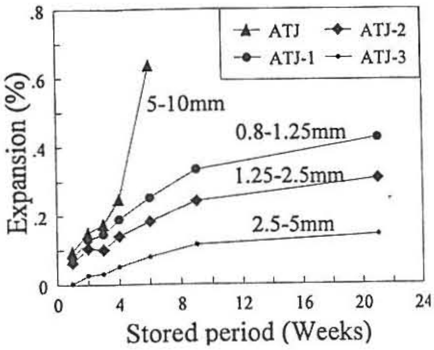

Fig. 1: The expansion curve of argillaceous dolomite from Tianjin

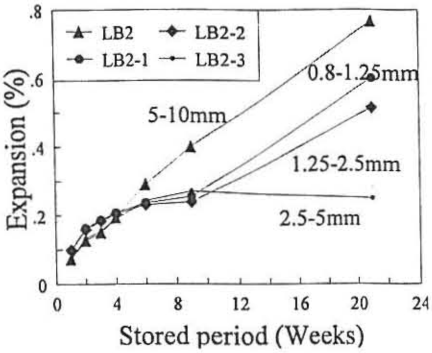

Fig. 2: The expansion curve of dolomitic limestone

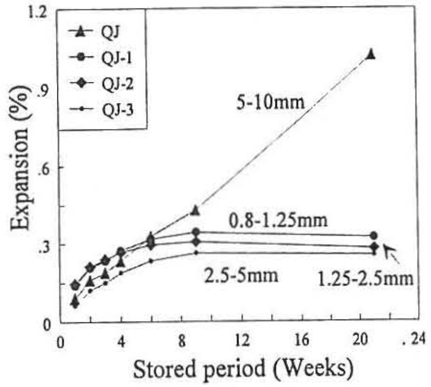

Fig. 3: The expansion curve of dolomitic limestone from Shandon

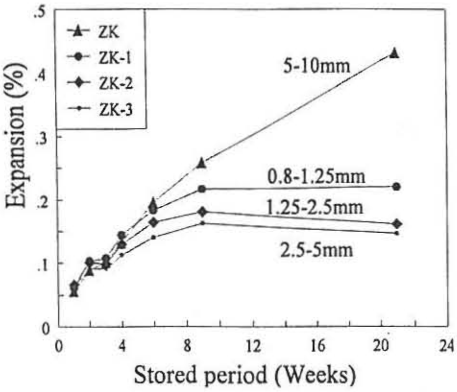

Fig. 4: The expansion curve of dolomitic limestone from Sichuan

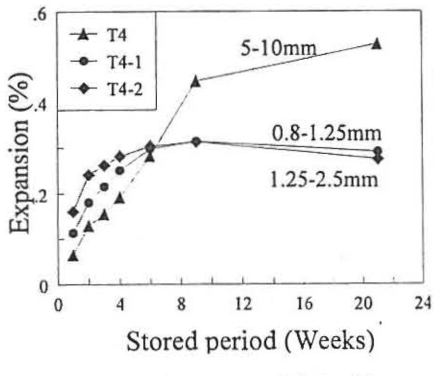

Fig. 5: The expansion curve of dolomitic limestone from Hebei

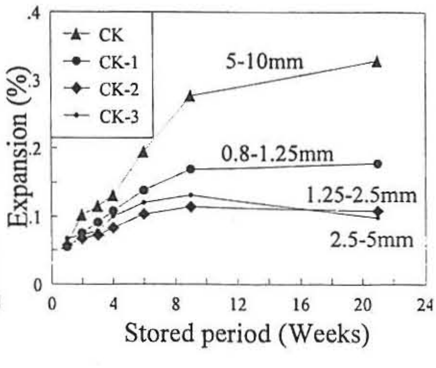

Fig. 6: The expansion curve of dolomitic limestone from Kingston

Rocks T4 and CK are dolomite limestone of Ordovician age. The result from T4 in Fig. 5 shows that expansion increases with decrease of particle size at early period, but becomes gently development after 4 weeks if using finer particle size. However, expansion of sample with 5-10mm shows a continued process, this also indicates the sensitive particle size. The expansion behavior of sample CK in Fig. 6 is similar to other rocks in this research. It can be concluded that 5-10mm of particle size is more sensitive for ACR expansion in the present research.

Fig. 7 is a summary of the results in this research. It shows the expansion curves of various reactive carbonate rocks. Some of them have shown their ACR reactivity and caused the field deterioration of concrete structures in many areas, e.g. Shandong, Tianjin, Hebei etc. The control sample C shows no expansion at any stored period in alkali solution at 80°C, which means that heat expansion at this temperature is very little. Normally, macrocrystal expand easily with increase of temperature, so other rocks are impossible to appear an obvious expansion.

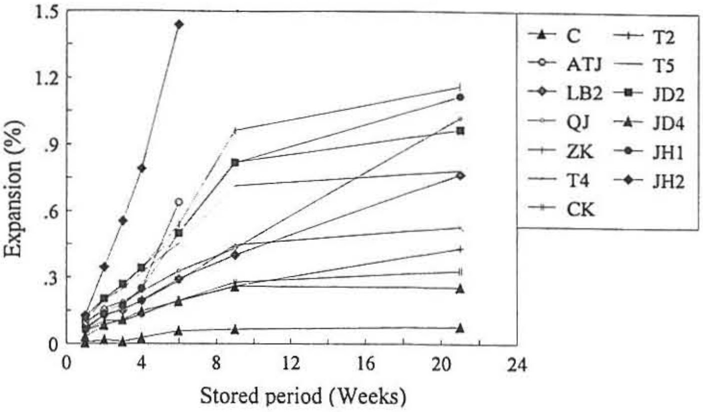

Fig. 7: The expansion curves of various carbonate rocks in alkali solution at 80°C (1M NaOH, 40 by 40 by 160 mm)

Various reactive carbonate rocks reveal the different expansion curves, their slopes and maximum values are related to their complex structures and individual chemical and mineral compositions. A common phenomenon can be seen that the reactive aggregates with 5-10mm of test particle size always show a continued expansion. This leads us to consider how to identify the potential reactivity of carbonate aggregates. Through comparing with the autoclave method and their behavior in field concrete, it can be suggested that if the expansion of the micro concrete bar exceeds 0.1% at 4 weeks, this aggregate can be judged to be alkali carbonate reactive.

This judgement can be confirmed by the behaviors in the field concrete structures of the test aggregates. The rocks WB, JH, Z and CK from Shandong, Heber, tianjin and Kingston etc have caused the deterioration of airports, bridges, pavements, railroad ties and other concrete structures. Furthermore, this judgement is consistent with the autoclave method proposed previously by the authors. It may be reasonable that the test period should delayed to 6 weeks or more for very important engineering (e.g. Three Gorges Dam in China), which have to be durable for several hundred years. It is noted that this judgement naturally needs to be confirmed by the testing with more kinds of aggregates and by other researchers.

Influence of Test Temperature on ACR Expansion

As we all known, there are two major ways to accelerate alkali-aggregate reaction, that is enhancing the content of alkali in system and increasing reaction temperature. It is noted, however, that the increase of test temperature must not change the nature of reaction products, and not change the process of cement hydration and AAR. At 80°C, it is well known that the nature of hydration products and the process of hydration will not be changed, only the rate of process will be accelerated. It is necessary to compare the behaviors of ACR in 1 M NaOH solutions at 80°C and 40°C.

Fig. 8 shows a comparison of ACR test at 80°C and 40°C with typical carbonate reactive CK and inert NJ (pure dolomite). It is clear that the inert aggregate NJ does not show expansion at higher or lower temperatures, this means that the present test procedure does not cause miss-judgement due to a heat expansion. On the other hand, standard reactive aggregate CK shows the same expansion curves at 80°C and 40°C. It can be believed that increase of temperature does not change the process mechanism of alkali-carbonate reaction and the nature of the products. Therefore, the test temperature of 80°C is reasonable for identification identification of the potential ACR reactivity of aggregates.

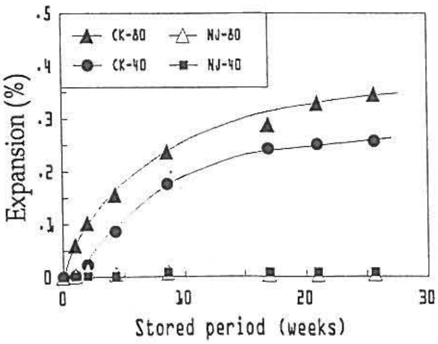

Fig. 8: A comparison test for typical reactive and inert rocks at 80°C and 40°C.

Influence of Cements on ACR Expansion

The alkali content of cement is normally believed to be an important factor in controlling alkali-aggregate reaction. The results of comparing test for low- (0.52% Na_2Oequiv.) and high- (1.24% Na_2Oequiv.) alkali content of cements at 80°C and 40°C are shown in Fig. 9 and Fig. 10. Obviously, under the condition of same total alkali content, mortars with low-alkali cement is favorable to the expansion of ACR. This phenomenon is also frequently found in ASR test. Therefore, It is necessary to stipulate the low-alkali content cement as a standard one, because high-alkali cements may sometimes show an apparent expansion during test period. At the same time, the expansion of pure cement paste is needed to be tested, and must be less than 0.002%. This consideration is specially emphasized for the Chinese situation because high-alkali cements are very common.

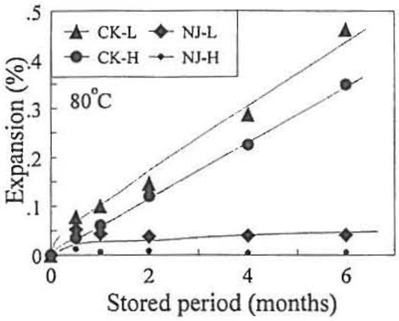

Fig.9: Comparison test for low and high alkali cements at 80°C (40 by 40 by 160 mm).

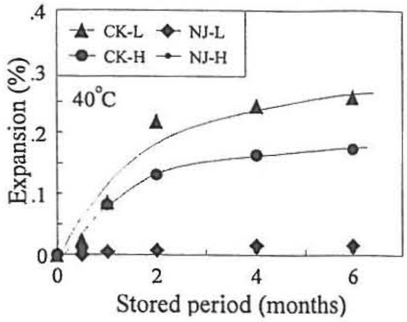

Fig.10: Comparison test for low and high alkali cements at 40°C (40 by 40 by 160 mm).

Evidences of Deterioration of Samples due to ACR Expansion

The tested samples were examined by microscopy. Fig.11 shows the mineral structure of rock, and cracking after 6 weeks of stored period. This mineral structure is similar to CK, it consists of 20-60mm dolomite crystals. The determination of ASR shows it non-reactive. After 6 weeks of treatment in alkali solution, all specimens were failed by cracking. This fact illustrates that the cracking is caused by ACR expansion, not by other factors.

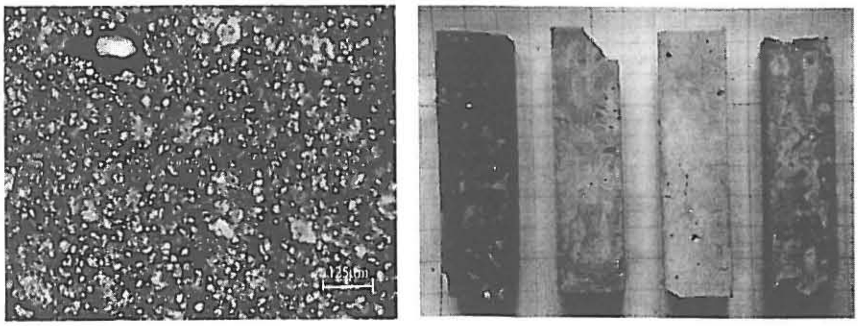

Fig. 11: Mineral structure of ATJ rock and its cracking of mortar (6 weeks).

CONCLUSIONS

1. The sensitive particle size for identifying the potential alkali-carbonate reactivity is 5-10mm in the present research. The mechanisms of ACR at 40°C and 80°C are usually same, the increase of test temperature does not influence the validity of judgement of ACR reactivity for carbonate aggregates.

2. The low alkali cement shows higher expansion than high alkali cement, and is favorable to enhance ACR process and may be stipulated as the standard one in this method.

3. This research offers a theoretical support for the new accelerated method for determining the potential alkali reactivity of carbonate aggregates. It needs to be internationally examined by more aggregates, engineering and researchers.

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