

# ASR in mortar bars containing silica glass in combination with high alkali and high fly ash contents

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## Abstract

In the paper, the problem of ASR in mortar systems with high contents of alkali and fly ash is studied. The results show that the danger of ASR exists in this system which it is different from ordinary plain cement system because in these systems, serious ASR was accompanied by great expansion of the specimens studied. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** High alkali content; Fly ash cement; ASR

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## 1. Introduction

A lot of research has shown that fly ash may inhibit ASR when its content is larger than 25%. But, the higher content of fly ash will affect the early performance of materials. In order to solve this problem, a large quantity of activator or early strength agent is often used. These admixtures are generally alkaline substances or alkali salts. Adding these substances will lead to a large quantity of alkali in the concrete. On the one hand, incorporating a large quantity of fly ash may inhibit ASR. On the other, higher alkali content may promote ASR. Thus, it is not clear whether ASR will occur under the condition of high alkali content and high fly ash content. There is only very little published information on such systems. This paper reports the results of a study undertaken to help understand the system of high fly ash high alkali concrete more clearly.

## 2. The relation of ASR expansion to alkali content

1. *The relation of the expansion of mortar bar to the alkali content of cement:* The alkali content of cement

and fly ash used in the experiment is shown in Table 1.

Silica glass is used as aggregate in the experiment, and its particle size is 0.15–0.80 mm. The ratio of cementing material to aggregate is 10, and the ratio of water to cementing material is 0.35.

In the experiment, the alkali content of cement is adjusted with added KOH to mix water. The specimens are cured by autoclaving at 150°C in 10% KOH solution or in saturated wet air at 70°C.

Fig. 1 shows the results obtained by Chinese autoclave method. It indicates that though adding fly ash markedly decreases expansion, the expansion of mortar bar with 30% fly ash increases with the increase of the alkali content of cement. Within the alkali content of the experiment, no pessiium was observed in the presence of fly ash.

Fig. 2 shows the expansion result for specimens cure for six weeks in saturated wet air at 70°C. They are basically consistent with the results of autoclaved experiments.

2. *The relationship between the expansion of mortar bars and the total alkali content of binder (cement + fly ash):* In the binder with high content of mineral admixture, some alkaline activator is often added. The content of activator is usually calculated in terms of the sum of binder. Adding these activators can promote the reaction of fly ash, and may lead to the reaction of alkali

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Table 1

The alkali contents of cement and fly ash

Materials	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)	Na <sub>2</sub> O <sub>eq</sub> (%)
PC	0.27	0.40	0.53
FA	0.37	0.66	0.80

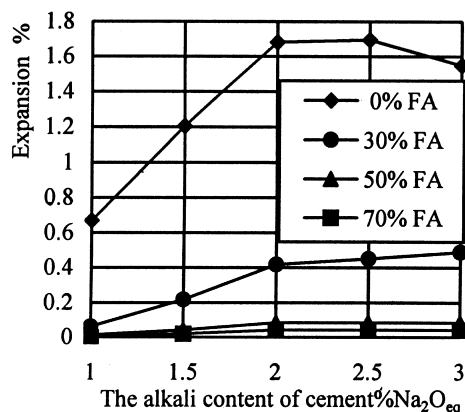


Fig. 1. The relationship between the expansion of mortar bars and the alkali content of cement under the autoclaved condition.

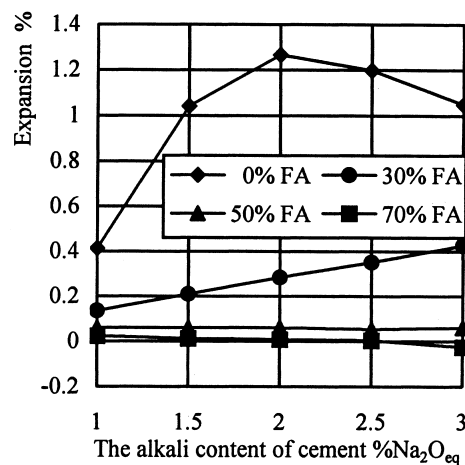


Fig. 2. The relationship between the expansion of mortar bar and the alkali content of cement under the condition of curing at 70°C for 6 weeks.

with the active component in aggregate at same time. Thus, the effect of alkali on reactive aggregate should be taken into account when fly ash is activated.

The relationship between the expansion of mortar bars and the total alkali content of binder is shown in Fig. 3. For convenience of casting, the ratio of water to cementing material is raised to 0.4.

The result indicates that if the content of fly ash is 0%, the maximal expansion is obtained when the total alkali content of binder is 2–3%; if the content of fly ash is 50%, the maximal expansion is obtained when the total alkali content of binder is 4%; if the fly ash content

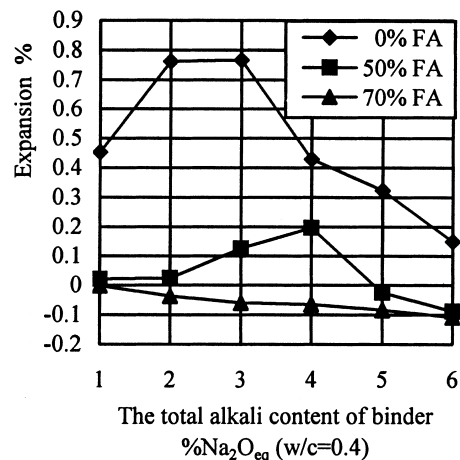


Fig. 3. The relationship between the expansion of mortar bar and the alkali content of binder under the autoclaved condition.

is 70%, the expansion decreases with the increase of the total alkali content of binder. The specimens will show obvious shrinkage when the alkali content is higher.

### 3. ASR under high alkali content and high fly ash content

Observing the specimen with 50% fly ash under stereomicroscope, it can be discovered that there are cracks in all specimens that the total alkali content of binder is higher than 3% (see Fig. 4(a) and (b)). For the specimen with 70% fly ash, a silica glass bar was embedded into the mortar bar. The specimen is cured with others, and polished to reveal the glass bar. The reaction of the glass to alkali is observed by stereomicroscope (see Fig. 4(c) and (d)). It shows that for the specimen with 70% fly ash, the side of glass bar is intact when the alkali content of cementing material is 1%. This indicates that the glass bar has not reacted to alkali. When the total alkali content of binder is 5%, the side of glass bar is obviously etched by alkali. Under the condition of very high alkali content, fly ash can retain only a part of alkali, and surplus alkali may still react with reactive aggregate. Gifford and Gillott [1] studied ASR and ACR in activated blast furnace slag cement concrete. The activators used in the study were both Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SiO<sub>3</sub>, and the content was 6% Na<sub>2</sub>O<sub>eq</sub>. The results indicated that for ASR, the expansion of activated blast furnace slag cement concrete is smaller than that of ordinary Portland cement; but for ACR, the expansion of activated blast furnace slag cement concrete is larger than that of ordinary Portland cement (see Table 2). These results also proved that the mineral admixture had not retained all alkali of the activator, a part of alkali reacted with the active component of aggregate.

Since ASR occurs under the condition of high alkali content and high fly ash content, why the specimen not

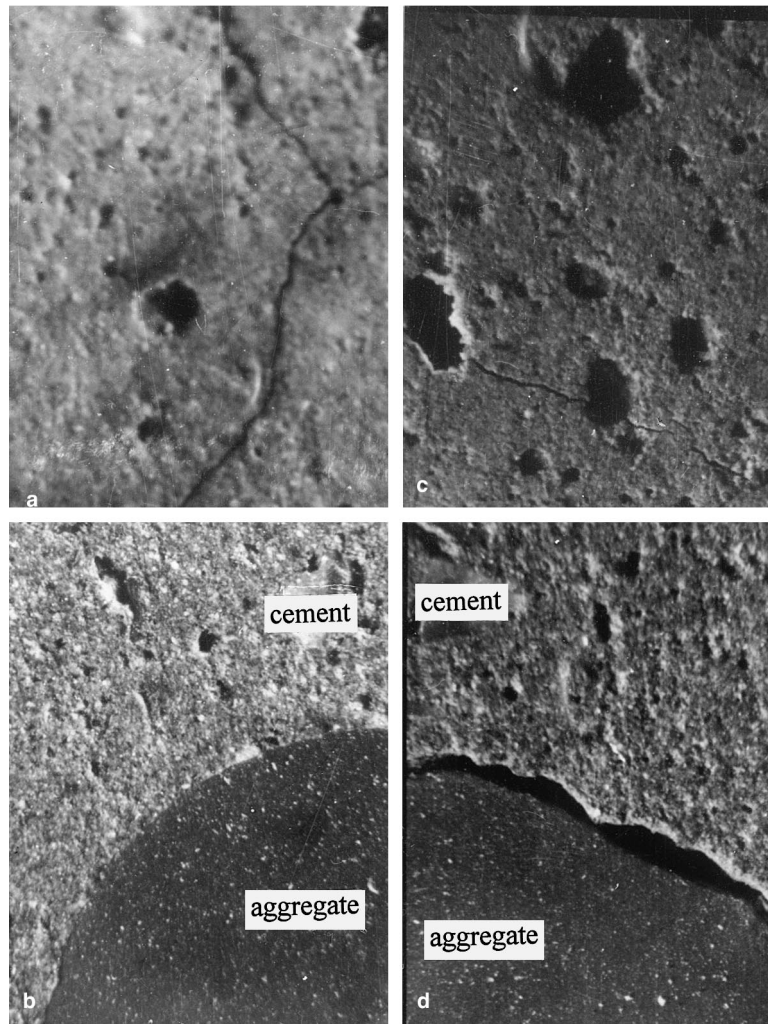


Fig. 4. The observational results by stereomicroscope: (a) The alkali content of cementing material is 4%, the fly ash content is 50%; (b) The alkali content of cementing material is 6%, the fly ash content is 50%; (c) The alkali content of cementing material is 1%, the fly ash content is 70%; (d) The alkali content of cementing material is 5%, the fly ash content is 70%.

Table 2  
Gifford and Gillott's experimental results

Aggregate	Expansion (%)					
	N <sup>a</sup>	P <sup>b</sup>	S <sub>1</sub> <sup>c</sup>	S <sub>2</sub> <sup>c</sup>	V <sup>c</sup>	B <sup>c</sup>
OPC	0.033	0.305	0.125	0.192	0.089	0.124
Na <sub>2</sub> CO <sub>3</sub> , ABFSC <sup>d</sup>	0.023	0.720	0.024	0.085	0.032	0.042
Na <sub>2</sub> O.SiO <sub>2</sub> , ABFSC <sup>d</sup>	0.030	0.617	0.021	0.082	0.028	0.059

<sup>a</sup> Non-reactive aggregate.

<sup>b</sup> Reactive carbonate aggregate.

<sup>c</sup> Reactive siliceous aggregate.

<sup>d</sup> Activated blast furnace slag cement.

only does not expand markedly, but yields larger shrinkage? Mingshu Tang even pointed out [2] that the expansion of mortar bar increases with the alkali content of cement. But when the alkali content of cement increases to a definite quantity, the expansion does not increase continuously, instead it decreases. This is

caused by the decrease of the viscosity of reaction product with the increase of its Na<sub>2</sub>O/SiO<sub>2</sub>. Urhan pointed out [3] that the viscosity of alkali-silicate colloid increases with the increase of the mole ratio of SiO<sub>2</sub>/Na<sub>2</sub>O<sub>eq</sub> and decrease of the content of H<sub>2</sub>O. For the reaction product of alkali-calcium-silica, its viscosity increases with the increase of the content of CaO. The expansion of concrete is attributable to the expansion of solid N-C-S gel instead of low viscous one. It may be seen from this that the expansion caused by ASR depends on not only its reaction degree but also the property of reaction product.

The product of ASR is actually a series of alkali-calcium-silica gels, differing in the proportion among alkali, calcium and silica.

It is due to the different proportion among the three components resulting in the difference of the properties of the reaction products. The entrance of alkali makes

the viscosity of the reaction product decrease, but the entrance of calcium makes it increase. There is a transition state from pure alkali–silica gel to C–S–H gel not containing alkali. The transition in components results in a change of the reaction product property from flexibility to stiffness, and also results in a change of the quantity absorbed water in the gel from high to low.

ASR expansion is related closely to the property of reaction product. With the increase of the alkali content of cement, the quantity and the alkali content of the reaction product increases. This will result in the increase of the expansion. But it will also make the viscosity of reaction product less. Thus, if the alkali content is very high, it is easier for the gel to flow from the surface of aggregate where it is formed to a pore. It may even flow out the surface of specimen. This will reduce the expansion. It is because of these actions that there is a pessimum point on the curve of the relationship between ASR expansion and the alkali content. This point shows that the more the reactive component in the aggregate reacts with alkali, gel with greater expansion potential, which does not readily flow away, is formed.

Some research showed that fly ash retain alkali. Because of this action, a large quantity of alkali reacts with fly ash particles. This reduces the alkali aggregate reaction. The surface property of the fly ash changes from acid to alkaline with absorption of alkali and its potential for alkali absorption will be reduced. That is to say that fly ash has a limited binding capacity for alkali. If the alkali content is very high, a part of alkali cannot be binded by fly ash particle, and it will react with the reactive component of aggregate. In general, the alkali content of cement is not very high. Thus, the replacement of cement by 50% fly ash may prevent expansion of the mortar bars. If the alkali content is so high as to exceed the binding capacity of fly ash, ASR will occur. In this research, under the circumstance of 50% fly ash, the expansion is 0.151% when the total alkali content of binder is 3%  $\text{Na}_2\text{O}_{\text{eq}}$ , 0.214% when that is 4%  $\text{Na}_2\text{O}_{\text{eq}}$ , and a crack appears. When fly ash content is 70%, the reaction of alkali with aggregate is also seen at higher alkali content by stereomicroscope. These experimental results show that ASR occurs unavoidably if the alkali content has exceeded the binding capacity of fly ash.

On the other hand, because the CaO content of fly ash is lower than that of cement, adding fly ash can reduce the CaO of the system. This will effect the quantity of CaO in alkali–calcium–silica gel, which will also effect the property of the reaction product and the expansion behavior of ASR. When fly ash content is 30%, the CaO content in the system is still higher. If the alkali content is higher, the alkali, which cannot be absorbed fly ash, will react with the reactive component of aggregate, and more CaO enters the reaction product.

It will result in larger expansion. When fly ash content is 50%, the alkali which cannot be absorbed by fly ash may react with the aggregate, but there is only a little of CaO to enter the reaction product. If a large quantity of alkali reacts with the aggregate but the CaO entered the reaction product is less, the ratio of alkali to calcium in reaction product is higher, and the viscosity of the reaction product is lower. This kind of reaction product will flow into the pore, or seep out the surface of the specimen, and makes no contribution to the expansion. Thus, less expansion is shown. When fly ash content is 70%, CaO hardly enters the reaction product. The reaction product is mainly the gel with low viscosity, and it does not cause expansion. Moreover, because of the dissolution of the active component of aggregate in the alkaline solution with high concentration and the loss of a large quantity of the reaction product with low viscosity, larger shrinkage results. This may be seen in Fig. 3.

Fig. 5 is the results observed by SEM. When the alkali content was very high, more serious reaction has also occurred around the aggregate even if a large quantity of fly ash was added. Fig. 6 is the results of the observation by SEM and the analysis by energy spectrograph to the reaction product around aggregate. It may be seen that the formed product is mainly the N–C–S gel contained more alkali.

In order to understand further the action of alkali under the different alkali and fly ash contents, the energy spectral analysis is made around the fly ash particle and aggregate particle. Figs. 7 and 8 show the results. The alkali distribution around fly ash particle increases with the increase of the total alkali content of binder. But, for two specimens that the total alkali content of binder is 4% and 6%, respectively, the difference of the alkali distribution is not large. Raising fly ash content from 50% to 70%, the alkali around fly ash particle decreases markedly when the total alkali content of binder is 1%, but has not a large change when the total alkali content of binder is 6%. These results demonstrate that the absorption of alkali by fly ash is finite. It may be seen from the alkali distribution around aggregate that when the total alkali content of binder is lower, there is only very little alkali around aggregate because of the absorption of alkali by the fly ash. When the total alkali content of binder is higher, the alkali around fly ash has been saturated, and a large quantity of alkali moves toward aggregate and reacts with the active component of aggregate.

When the fly ash content is 50%, though it is shown in Fig. 3 that the expansion of specimen with 6% alkali is less than that with 4% alkali, it may be known from Fig. 5 that the alkali around the aggregate is higher when the alkali content is 6% than 4%. It may be discovered from energy spectral analysis that the  $\text{K}_2\text{O}/\text{CaO}$  of the reaction product is higher when the alkali content

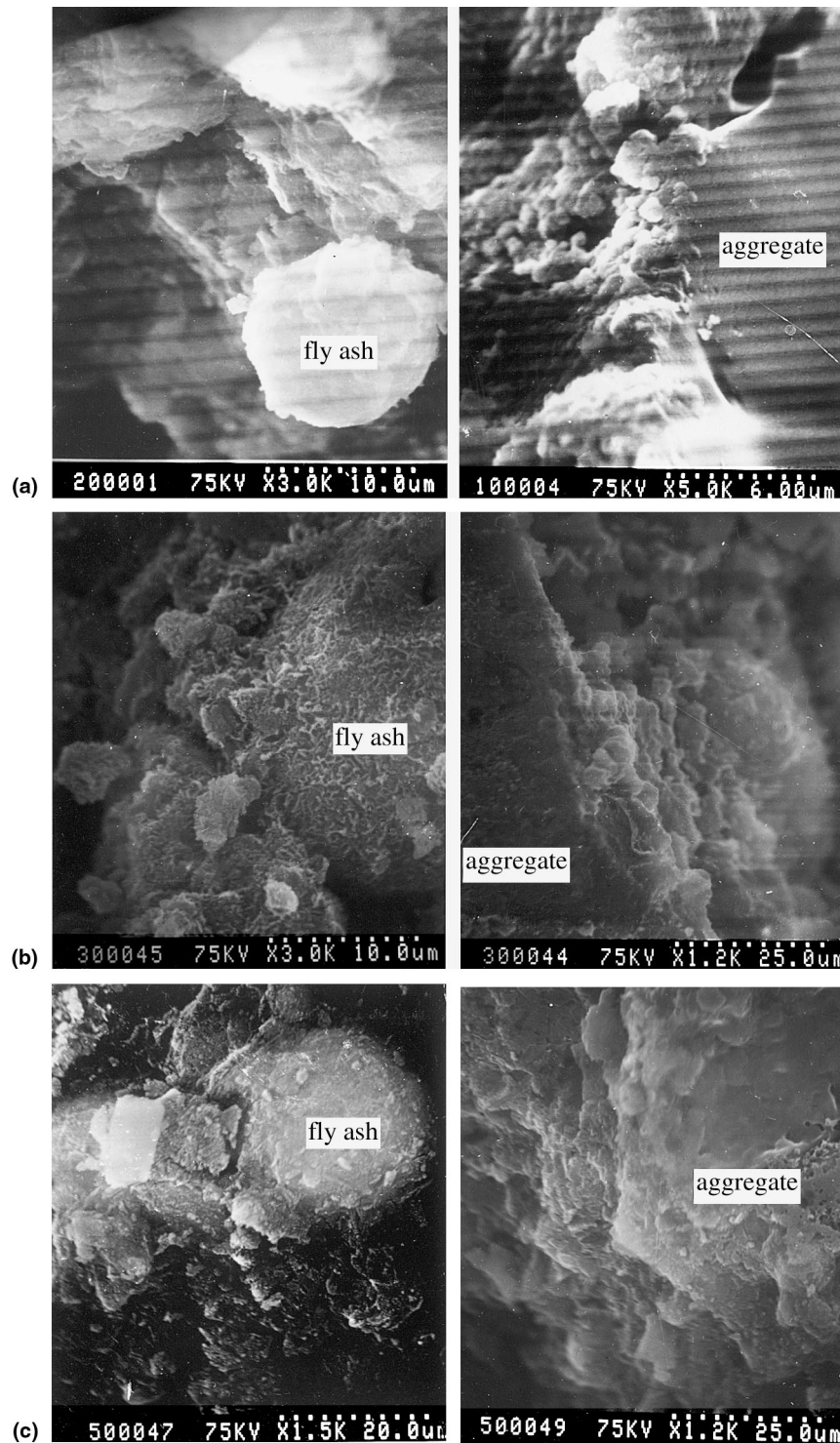


Fig. 5. The observation results by SEM: (a) The specimen that the fly ash content is 50% and the total alkali content of binder is 4%; (b) The specimen that the fly ash content is 50% and the total alkali content of binder is 6%; (c) The specimen that the fly ash content is 70% and the total alkali content of binder is 6%.

is 6% (see Fig. 9). This demonstrates that the expansion of mortar bar depends on not only the quantity of the reaction of alkali to aggregate but the property of the reaction product.

The experimental results and theoretical analysis show fly ash effects not only expansion due to ASR and alkali absorption, but also the composition and properties of the reaction products, by decreasing the CaO



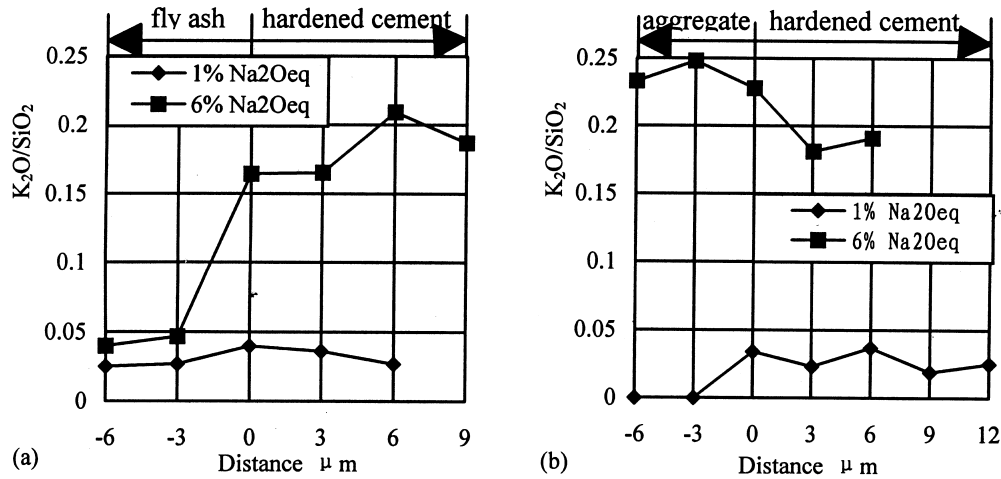


Fig. 8. The alkali distribution when fly ash content is 70%: (a) The alkali distribution around fly ash particle; (b) The alkali distribution around aggregate particle.

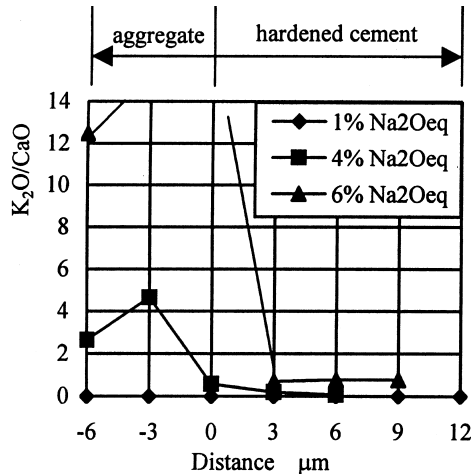


Fig. 9. The influence of the total alkali content of binder on the  $K_2O/CaO$  in the interfacial area.

content in system. Under normal circumstance, the total alkali content of binder is finite, and the affect of fly ash is mainly the absorption of alkali. But for the system containing considerable alkaline activator, the harm of AAR should still be noticed though a large quantity of fly ash is added. Further studies are needed to determine how the action of fly ash in this system should be evaluated and how its durability is.

#### 4. Conclusions

By above analysis and research, some knowledge of ASR in systems with high alkali and high fly ash contents were obtained. Following conclusions may be shown:

1. Under the conditions of high alkali content and high fly ash content, there is still the danger of ASR.
2. ASR expansion depends on not only the amount of ASR but also the property of the reaction product. Under the condition that both of the alkali content and the fly ash content are very high, it is possible that large expansion does not occur though considerably ASR has occurred.

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