

**MECHANISM OF REACTIONS INVOLVING
BRITISH CHERT AND FLINT AGGREGATES**

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1. ABSTRACT

The present understanding of alkali-silica deterioration processes is based almost entirely on research conducted using opal aggregates. Opal has not been used for concrete aggregate in the UK, and standard reactivity tests are unsuitable for British cherts and flints, which account for most occurrences of ASR. Research indicates that there are fundamental differences between the reaction of cherts and flints, and that of opals, both in terms of reactive mineral constituents and reaction processes. Opals are highly reactive due to their mineralogy, whereas cherts and flints are essentially monomineralic and possess low intrinsic reactivity. Chert and flint reactivity is dictated by the ability to concentrate reactants from the surroundings, and this is a function of primary micropore structure. Reaction occurs by direct solution at micropore walls once internal alkali hydroxide concentration exceeds a threshold level. Crushing the particles disrupts the micropore structure and destroys the ability to concentrate reactants, rendering the aggregate innocuous at normal concrete alkali contents.

These factors account for several features of chert and flint reactivity such as the absence of a pessimum and the apparently anomalous behaviour in direct chemical and mortar bar tests. The ability to concentrate reactants also implies a potential for reaction at much lower concrete alkali contents than opals, and it is suggested that the 0.6% / 3 kg/m³ total alkali limits may be too high to prevent reaction. There is strong evidence that potassium is the most aggressive alkali species; sodium did not participate in the reaction in any of the concretes containing chert or flint which were tested at ambient temperature. However, sodium may enter the reaction product soon after formation, and can therefore affect expansion behaviour. An explanation for the apparent conflict between deleterious expansion and the presence of highly mobile reaction product is suggested.

2. INTRODUCTION

It has traditionally been assumed that because a reaction involving aggregate occurs between alkali hydroxides and some form of silica, and produces an expansive alkali-silica gel reaction product, the mechanism of deterioration must be the same as that with other alkali-silica reactive rocks. The first reported occurrence of ASR involved opal [1], and most subsequent research into reaction mechanisms has therefore used this aggregate. Results have been universally applied in the evaluation and control of reactions involving other aggregate types, and alkali concentrations found to be "safe" with opals have become enshrined in national standards. However, over the last 14 years or so the validity of these assumptions has been questioned in the case of reactions involving rocks such as argillites and greywackes, because the physical appearance of deterioration is so different from that of classic ASR. More recently, numerous authors have reported that "standard" tests developed with opals fail to predict the reactivity of other aggregate types. This is particularly so in Britain, where no instances of reactions with opal have been identified, and the majority of reported occurrences of ASR involve chert or flint*. No British aggregates in known use are classified as deleterious by the ASTM mortar bar test, including aggregates of the types known to have caused deleterious reaction in the field [2], whereas the ASTM rapid chemical test proves positive for most British cherts or flints although many are not reactive in normal use [3]. In addition, practical evidence suggests that many British aggregates have reacted at concrete alkali contents significantly less than the 3 kg Na₂O equivalent per cubic metre of concrete which is normally accepted as the safe maximum, and that few, if any British cherts and flints display a pessimum. To investigate the reasons for these apparently anomalous trends, a detailed study was made of reaction and expansion patterns in concrete containing British chert and flint aggregates [4]. Factors which influence the rate and extent of deterioration were considered, and findings were compared with the behaviour of classically reactive opal aggregates.

3. COMPARISON OF CHERT AND OPAL REACTIONS

Diamond [5] observed that any variety of silica can be broken down and converted to alkali-silica gel, given a sufficiently aggressive environment and sufficient time. The major factor controlling reactivity was considered to be crystal structure; minerals with a disordered lattice are rendered more liable to attack, and susceptibility is increased if the lattice structure is partially hydrated, as is the case with opal.

The reactive components of cherts, flints and opals are microcrystalline quartz, tridymite and cristobalite (polymorphs of silica), chalcedony (cryptocrystalline silica) and opal (amorphous silica). These components may be present in differing proportions in each of the rock types, and there is considerable variation in the degree of reactivity shown by each. At least four categories of opal have been recognised on the basis of mineralogy [6,7], but all are characterised by a high proportion of forms of silica other than quartz, and are therefore highly reactive with cement alkalis. Beltane opal, which is known to be extremely reactive and has widely been used as a "standard" aggregate for the

* The term "flint" is used here to describe the variety of chert occurring in or derived from chalk deposits.

study of ASR, is reactive principally because of its disordered opal content (46%), but significant reactivity is also shown by cristobalite and tridymite, which constitute a further 26 to 30% of the rock [8]. Other opals contain less reactive material, but all types have a similar dense microstructure, and reaction typically manifests itself by the formation of a gel reaction rim at particle margins, although in some cases reaction may occur throughout the particles.

In contrast, cherts and flints generally have a porous microstructure, and contain little or no highly reactive mineral components. Most Danish flints are reactive under appropriate conditions in the presence of sufficient alkalis, but the rate of expansion in mortar samples differs markedly for each flint type [9]. Opaline flints were found to react very quickly, whereas chalcedonic varieties reacted more slowly, and only if porous. Some UK flints contain inclusions of chalcedonic silica [10], but all British cherts and flints examined in the present study were petrographically and mineralogically indistinguishable, being composed almost exclusively of microcrystalline quartz. In practice, few if any British flints are reactive under normal conditions, but unlike opals, such differences in chert and flint reactivity cannot be due to differences in the type and/or proportion of highly reactive forms of silica which are present. In addition, the classic ASR model predicts that given sufficient water and alkalis, reactions involving such monomineralic lithologies will proceed until all reactive aggregates are converted to gel. There is no evidence that this occurs in the field, and experiments on deteriorated structural concrete containing reactive chert demonstrated that ASR can be exhausted even when significant quantities of water, alkali hydroxides and unreacted aggregate are present [4]. It is thus clear that factors other than mineralogy must have a significant influence on the reactivity of cherts and flints, and the mechanism of reactions involving these aggregates is therefore reviewed.

4. MECHANISM OF REACTIONS INVOLVING CHERT AND FLINT

The attack of siliceous aggregates by alkali hydroxide solutions is generally considered to be a two-stage process involving the reaction of acidic silanol groups followed by breakdown of siloxane bridges [11,12]. It is argued that this produces a progressive "loosening" of the lattice structure which increases its capacity to absorb alkalis and water, leading eventually to complete breakup and the formation of a weakly bonded alkali-silica gel or sol. Samples of reactive opal and flint were analysed by solid-state ^{29}Si NMR before and after reaction with alkali solutions using both MAS and ^{29}Si - ^1H CP techniques to obtain precise information about changes in lattice structure. In all cases, spectra obtained before and after reaction were almost identical, and no evidence of structural weakening or hydration was detected. This clearly indicates that reaction of these lithologies does not involve structural breakdown, but is a simple solution process which occurs without weakening and hydrating the lattice of the remaining particles.

Unlike opals, petrography indicates that the reaction of chert and flint aggregates generally occurs throughout the body of the particles, and is concentrated at micropore walls. Reaction rims are rarely formed except in the smallest particles. Particles of chert and flint derived from natural sands and gravels characteristically have a well-developed concentric structure with a finely microporous rim enclosing a core of more coarsely microporous material, and such particles generally contain a concentration of alkalis at their centre which is many times greater than in the surrounding paste. Such concentrations do not occur when the particles are crushed or broken, which suggests that the physical structure of particles is instrumental in the concentration process [13]. Each variety of chert and flint examined in the present study possessed this ability to concentrate alkalis, and no consistent differences in the selectivity for each alkali species were noted. Differences in the reactivity of intact particles must therefore be due to differences in susceptibility to attack rather than to inability to assimilate reactants. Since all varieties were mineralogically indistinguishable, it is considered that reactivity is probably a function of the micropore system, such as size distribution. It is suggested that solubility is increased when pore diameter is smaller, due to the higher surface energy or charge density on the pore walls. This is in accord with findings that flint reactivity correlates with an abundance of smaller micropores [14].

Most reaction models have assumed that reactants reach reacting particles by simple diffusion, and theories such as osmosis have been invoked to account for the partition of ions into reactive aggregates. However, the concentration mechanism cannot be passive diffusion, because by definition diffusion cannot operate against a concentration gradient [15]. Alkali concentration must therefore be an active process, and French [13] proposed a mechanism similar to capillarity. However, capillary action applies only to fluids, which implies that ions must enter reacting particles in solution. Once capillary pressure is attained, further movement would be unable to occur without fracture of the particle to allow the escape of fluid, and this mechanism cannot therefore account for the high alkali concentrations observed. It is thus proposed that attraction and concentration of alkali ions is not achieved by capillarity, but is due to intrinsic attraction of the silica lattice caused by surface charges resulting from exposed oxygen and silicon radicals. In dense particles such as opals this charge will be concentrated at the aggregate perimeter, and reactants will be drawn from the environment to particle surfaces, where they react at low concentrations due to the high intrinsic reactivity of such lithologies, forming reaction rims. In contrast, the attractive force of microporous aggregates such as chert and flint will be much greater than that of opals due to the high internal surface area, and high alkali concentrations will build up within particles. However, since this attraction will not diminish if particles are broken, this process alone cannot account for the differences in alkali concentration observed between intact particles and those in which the outer rim of micropores has been breached. It is thus considered that the finely microporous rim of intact particles acts as a semipermeable barrier to the movement of alkali and hydroxyl ions. These are drawn inside particles by the strong attractive force, but their exit is impaired by the small size of micropores in the rim, so that a high concentration builds up. Differences in the reactivity of chert and flint particles are attributed to the low intrinsic reactivity of the mineral component in these lithologies, which is unable to react until a threshold reactant concentration much higher than that required by opals is achieved. This also explains why cherts and flints rarely form reaction rims, since alkali concentrations in normal pore solutions are below the reaction threshold. It is suggested that broken particles or those lacking the necessary micropore structure are unable to concentrate alkalis sufficiently to achieve the threshold and cause

reaction, but once internal concentration exceeds the threshold, the alkali solution begins to corrode the micropore walls. Reaction is not considered to involve the development of a hydrated layer at the pore walls which would neutralise the surface charge, but is envisaged as a plucking of silicon and oxygen atoms from the exposed ends of the lattice, followed by neutralisation in solution, leaving more free radicals exposed. Thus the potential for attraction of reactants remains, and alkali assimilation continues.

Differences in the reactivity of various cherts and flints are not explained entirely by differences in their ability to concentrate reactants; intact, unreacted aggregate particles containing a high concentration of alkalis are not uncommon. Reactivity must therefore be due to the presence or absence of a reactive component in the aggregate, but since the cherts and flints examined in the present study are monomineralic, this reactive component must represent a physical difference between reactive and non-reactive material. Structural concrete samples in which ASR was exhausted were exposed to a strong mixed alkali hydroxide solution, and deleterious reaction was not rejuvenated. It is concluded that since the aggregates had previously reacted, the reaction must have halted because the reactive component became exhausted. Since reaction is concentrated at micropore walls in these rocks, the factors controlling reaction are considered to relate to enlargement of the micropore system. It is suggested that differences in the charge or surface energy on pore walls of different radii affect their susceptibility to attack, so that reaction can only occur at the walls of pores smaller than a certain size. Once solution increases the diameter of all micropores to this limiting size, reaction will stop. However, in the concrete tested, reaction was rejuvenated when samples were exposed to the same alkali solution at higher temperature, and it is concluded that the upper size of micropores susceptible to attack must therefore be temperature dependent. At higher temperatures a greater proportion of the internal surface of chert and flint particles is thus susceptible to attack, and reaction would be expected to continue at the higher temperature until all micropores are enlarged to the new limiting size, when equilibrium would be re-established.

Pessimism behaviour was originally described from opal aggregates, and is classically interpreted as the result of the availability of alkalis at the reaction site; if threshold alkali concentration cannot be achieved, no reaction and expansion can occur. With opals and similar reactive materials where ability to concentrate alkalis is limited, reactants can only be drawn from a certain distance surrounding the particles. The failure of classic reaction models to account for the lack of a pessimism with British flints and cherts is considered to be because the ability of such aggregates to attract reactants over considerable distances has been ignored. It is proposed that such materials are able to concentrate reactants so strongly that they are capable of extracting sufficient alkali hydroxides from the environment to exceed the threshold and cause reaction even when the concentration of alkalis in the environment is very low. Natural cherts and flints of the type examined in the present study therefore have no pessimism, and the magnitude of deterioration increases in direct proportion to the quantity of reactive aggregate in the mix. The process of alkali extraction is considered in many cases to be so efficient that most reactants in the concrete can be utilised, and the minimum alkali concentration necessary for reaction will therefore be much lower than that for classically reactive materials such as opal. This implies that the $3 \text{ kg/m}^3 \text{ Na}_2\text{O}$ equivalent limit calculated for concretes containing opal may be too high to prevent deterioration in concretes made with typical British aggregates. This is supported by many of the ASR-deteriorated structural concretes analysed in the present study, which mostly had total alkali contents substantially less than 3 kg/m^3 .

When concrete containing normally innocuous flint or chert aggregate is exposed to an external source of alkalis at ambient temperature, its behaviour will depend on aggregate properties. If the lack of reaction was due to the absence of micropores in the aggregate of the size susceptible to attack, the increased alkali levels will not cause reaction. However, if the lack of reaction was due to inefficiency of the aggregate at concentrating reactants, then raising the alkali concentration of the environment sufficiently will initiate reaction once the threshold necessary for reaction is reached. Investigations into a number of British aggregates showed that none caused expansion in mortar bar tests with normal high alkali cement, but reaction occurred in all cases when total cement alkalis were boosted to 2.4% Na_2O equivalent [16]. Under these conditions, normally innocuous Thames Valley flints were reactive, and showed a marked pessimism of 20%. This apparently anomalous behaviour is readily explained in terms of the reaction mechanisms outlined above. The normally innocuous nature of all aggregates tested was clearly due to their inability to concentrate reactants. By raising mix alkali levels sufficiently, the aggregates were made to react, but the requirement for particles to concentrate alkalis in order to achieve the reaction threshold was eliminated. Reaction thus became controlled by the concentration of reactants in the immediate vicinity of reacting particles, and was thus subject to the same factors which control the reaction of classically reactive aggregates such as opal. This explains why most British chert and flint aggregates produce a positive response in direct chemical tests such as ASTM C289, and yet none are classified as deleterious by the mortar bar test, since crushing the aggregate to the required grading for mortar disrupts the internal structure and destroys the ability of the particles to concentrate alkalis.

5. EFFECT OF DIFFERENT ALKALIS ON CHERT AND FLINT REACTIONS

Concretes containing reactive British chert were immersed in NaCl and KCl solutions. Results showed that Na^+ does not participate in the deleterious reaction of these aggregates at ambient temperature, and attack is due solely to the action of K^+ and OH^- . Na^+ did promote attack at temperatures above 38°C , but the resulting expansion was less than that produced by an equivalent concentration of K^+ . These results were confirmed by experiments with reactive concretes immersed in mixed alkali hydroxide solution. Analysis showed that the level of Na^+ in the solution decreased only marginally during the experiment, but K^+ concentration was reduced by 20%. This clearly indicates that the reaction resulted from the action of K^+ , leading to its selective removal from the solution. However, extensive microanalytical evidence from concretes containing reactive British aggregates indicates that sodium is often closely associated with degraded particles, and it is therefore suggested that this ion may enter the reaction product soon after formation, before it migrates from the generation site. A further experiment showed that when K^+ concentration in the test solution was

very low, Na^+ was assimilated from the environment, and the reaction product contained a high proportion of sodium silicates. However, this reaction was not deleterious, which suggests that the high-sodium gel may have been less disruptive than that containing more potassium.

An extensive study into the reactivity of Danish flints has been conducted using a technique which involves storing mortar bars in saturated NaCl solution at 50°C [17,18,19]. There is no doubt from published results that NaCl has an accelerating effect on damage, and it was proposed that OH^- necessary for reaction was derived by dissociation of $\text{Ca}(\text{OH})_2$, so that the presence of free portlandite in the concrete is a prerequisite for ASR. However, this clearly applies to situations where alkali ions are abundant but sufficient OH^- is not freely available for reaction. The proposed reaction mechanism therefore applies only to attack by alkali salt solutions, and the present work indicates that this mechanism is unlikely to operate at ambient temperature with NaCl solution. This implies that the application of de-icing salts to structures incorporating reactive cherts and flints of the type examined in the present study is unlikely to result in the initiation or aggravation of ASR (although the effect of Cl⁻ on buried reinforcing steel will still be detrimental). The localised deterioration observed below leaking expansion joints in such structures, for example, is considered to result primarily from the effect of increased mechanical and freeze-thaw damage due to the presence of the salt. It is suggested that the resulting increase in permeability then combines with the abundant moisture from the leaking joint to exacerbate ASR in the region.

Differences in the degree of reaction produced by Na and K have long been recognised [20], and are attributed to differences in the size of hydrated ions [18,21]. However, these differences have always been ignored, and equal molar concentrations of each species are always treated as equally aggressive. The measure of Na_2O equivalent has therefore gained universal acceptance as the standard method for expressing alkali content. The present study confirms earlier findings [20,21] that K^+ is more aggressive than Na^+ , and demonstrates that with certain aggregates, Na^+ may not cause reaction at ambient temperature. It is suggested that any apparent correlation between the reactivity of concretes made with aggregates of the type tested and alkali content expressed as Na_2O equivalent may be largely fortuitous, and results from the fact that the K:Na ratio of most cements is similar.

6. EXPANSION BEHAVIOUR

The term "alkali-silica reaction" is invariably used ambiguously to describe both the chemical reaction of susceptible aggregates, and the physical disruption caused by the reaction product. These two processes are clearly not synonymous, and are subject to different controlling factors, so that they interact in a complex fashion to produce the different patterns of deterioration observed. The ability of a particular aggregate to undergo deleterious reaction in concrete is therefore dictated both by its ability to react with the alkali hydroxides present, and by the efficiency of the reaction product at causing disruption. The latter depends on swelling properties of the gel, and the rate at which it can dissipate from the generation site, since this determines its ability to exert a swelling pressure on its surroundings.

Alkali-silica gels are colloidal solids in which the alkali-silica component forms a cross-linked network, and water is held interstitially as a disperse phase. Since the gel is of an ionic type, it is highly hygroscopic and absorbs large amounts of water from its surroundings, leading to very large expansions as it is accommodated in the gel network. Given sufficient moisture, swelling tends to continue until the chains of gel molecules are fully stretched, and if the charge density is high enough, the entry pressure of water may be sufficient to rupture the internal bonds. The gel structure then breaks down and a sol with much lower viscosity results. The physical properties which dictate the efficiency in disrupting concrete are viscosity and swelling pressure. The gel must exert a pressure of at least twice the tensile strength of cement paste to create a crack [22], and the ease with which this can occur will be dictated by the viscosity, since if the gel is too fluid it will permeate from the reaction site without causing disruption. Gel properties depend on its physical structure, which is in turn affected by composition, water content, temperature, confining pressure and dynamic loading. Because of the difficulty of obtaining sufficient natural alkali-silica reaction product for study, investigation into swelling properties has been limited to the study of synthetic gels. There is considerable literature on the properties of sodium silicates (water glass), and for this reason all research has concentrated on the system $\text{Na}_2\text{O}\text{-SiO}_2\text{-H}_2\text{O}$. Far less is known about potassium silicates, and possible differences in their behaviour in concrete have been almost universally ignored. In general, the relative size and charge of the cation strongly affect the characteristics of alkali-silica gels, since larger ions are held more strongly in the gel network [23,24]. The structure of sodium and potassium silicates is therefore fundamentally different; sodium silicates tend to have a lower degree of cross-linking than potassium silicates, and are generally less viscous and turn to sols at much lower water contents. The alkali:silica ratio has a critical effect on viscosity; studies with sodium silicates demonstrate that viscosity falls much more rapidly with an increase in water content when Na:Si is high than when the ratio is lower. Minimum viscosity for a given water content generally occurs when Na:Si is about 1. The viscosity of sodium silicates changes suddenly at relatively high water content, so that once water content rises to a critical level, a very small uptake of water will cause a rapid transition from gel to sol [24]. The practical implication of this phenomenon is illustrated by studies on synthetic sodium silicate gels [25,26], which frequently showed spontaneous liquefaction and loss of swelling pressure during test. A similar effect occurs with potassium silicates, but the effects are more pronounced [24].

A number of authors have argued that alkali-silica gel can only cause expansion and crack propagation when a solid or semi-solid [22,27,28,29]. Experiments conducted during the present study indicate that under certain circumstances, more fluid reaction product in the crack and micropore system may exert sufficient force to cause expansion, as suggested by others [30], but it is still considered that most damage is centred on the reaction site and occurs at an early stage of reaction. The observation that only K^+ is active at ambient temperature in the breakdown of the cherts and flints tested provides some evidence of how such a process may be possible. The initial gel formed from solution will be pure potassium silicate with a very low alkali:silica ratio and water content. Both of these factors imply that the gel will be

of a highly viscous and swelling type. However, Na⁺ is assimilated at an early stage, and some K⁺ may be lost soon after formation. The gel will therefore quickly become more fluid and escape from the generation site through the crack system. Since gel formation is a continuous process, expansion will thus be able to continue whilst reaction progresses, causing further disruption and crack propagation. This explains the apparent conflict between the exertion of swelling pressure which causes deleterious expansion, and the presence of highly mobile gel in cracks a long distance from generation sites. The reactivity of opals with Na⁺ at ambient temperatures indicates that the initial reaction product will be less viscous than that produced by British cherts and flints, but this is likely to be offset by the greater intrinsic reactivity of opal, which will therefore produce a greater proportion of gel than other aggregate types. This may explain how reactive British cherts cause severe disruption, and yet produce a smaller quantity of gel than might be expected.

It is generally assumed that expansion due to ASR correlates directly with the development of cracking. This relationship has been demonstrated in some studies on mortar bars [29], but the present work with deteriorated concretes from British structures indicates a generally poor correlation between the quantity of gel present, magnitude of expansion in accelerated tests, and the size and frequency of microcracks. The explanation is one of cause and effect; expansion is not due to microcrack formation as is always assumed, but rather cracking is the result of the release of stresses caused by expansion centred on reactive particles. Thus, the expansion of concrete and formation of microcracks will depend on the ability of the cement matrix to withstand the stresses developed by reaction; this will be dictated by intrinsic properties such as tensile strength, ductility, Young's Modulus and Poisson's Ratio. Some ductile concretes will therefore be able to expand without substantial crack development [31], whereas more brittle materials will expand in a series of steps as stresses are released by cracking [32]. Concretes where the cement paste is sufficiently ductile to accommodate the expansion of reactive particles will show neither expansion nor cracking; this behaviour was observed in cores from several dams in Britain where the cement paste was severely leached and recrystallized.

7. MAIN CONCLUSIONS AND IMPLICATIONS

1. Styles of deterioration developed by different aggregates are distinct. These differences are considered so great that they should be regarded as different types of alkali-silica reactions. At least three categories of reactive material are therefore recognised:
 - Dense aggregates with disordered silica or polymorphs of silica other than quartz, *e.g.* opal and glass
 - Microporous aggregates consisting principally of microcrystalline quartz, *e.g.* chert and flint
 - Rocks with finely-divided siliceous and silicate matrix, *e.g.* greywacke and argilliteRocks containing strained and finely granulated quartz may form an additional category.
2. The assumption that equal concentrations of Na and K are equal in effect is not valid. Alkali content expressed as Na₂O equivalent is therefore unsuitable as a measure of the potential for reaction.
3. The 0.6% Na₂O equivalent cement alkali and 3 kg/m³ concrete alkali limits established using opal aggregates may be too high to prevent deleterious reaction in concretes containing potentially reactive chert and flint, due to the strong ability of these aggregates to concentrate reactants.
4. De-icing salt contamination is unlikely to initiate or accelerate ASR in concretes containing aggregates of the type tested due to the inability of sodium to participate in the reaction at ambient temperature.
5. Presently accepted "standard" tests developed with opals for the assessment of ASR are unsuitable for use with other lithologies which have considerably different reaction mechanisms. Direct chemical tests give no indication of the ability of the reaction to cause physical damage, and will give particularly misleading results with cherts and flints, because the ability to concentrate reactants, which is the major control on their reactivity, is made redundant.

8. ACKNOWLEDGEMENTS

This study was conducted in the Geomaterials unit at Queen Mary College, University of London, England. I wish to thank Alan Poole for supervision, and Bill French and Jonathan Wood for discussions. Concrete samples were provided by Mott, Hay and Anderson Ltd., and Geomaterials Research Services Ltd. The first two years of this study were funded by a SERC CASE award in conjunction with Mott, Hay and Anderson Ltd. Subsequent research was conducted whilst working part-time for Geomaterials Research Services Ltd.

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