

A REVIEW OF ALKALI-SILICA REACTIVITY IN TURKEY: A CASE STUDY FROM IZMIR, WEST ANATOLIA

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Abstract

A review of the alkali silica reaction (ASR) history in Turkey is presented in this paper including case studies from the vicinity of Izmir. The first case of ASR in Turkey has been detected in the bridges that were built from mid-eighties to mid-nineties in this region. This paper includes some recent findings from detailed petrographic examination of ASR gel found in the concrete cores taken from these bridges and concrete alkali budgets estimation. It was no surprise that the map cracks in the concrete pavements of Izmir Adnan Menderes Airport was also due to ASR since they contain reactive sand and built in a similar period with the deteriorated bridges. ASR in the apron concrete was analysed by microstructural methods and concrete mix design was estimated. Today, non-reactive crushed limestone aggregate is used in concrete production in Izmir and no evidence of ASR is observed in the structures that were built after mid-nineties.

KEYWORDS: alkali silica reaction, Turkey, Izmir, concrete, microstructure

1 HISTORY OF ASR IN TURKEY

The earliest documentation on Turkish aggregate sources from alkali aggregate reaction (AAR) viewpoint was published in 1975 reporting that 30% of the concrete aggregates used in some dam projects were susceptible to alkali aggregate reactivity according to ASTM C289 (Chemical Test) method [1]. These reactive aggregates were used in concrete with low alkali cement or with the incorporation of fly ash. At those years, nearly 85% of the cement produced in Turkey might be classified as low alkali ($\text{Na}_2\text{O}_{\text{eqv}} < 0.66\%$), however after the conversion of wet system cement kilns into dry system kilns, the alkalinity of the cement produced in Turkey was significantly raised. Note that the alkali level of cement produced in the year 1996 was between 0.81% and 0.97% $\text{Na}_2\text{O}_{\text{eqv}}$ and today these levels are still in the same range. Still no case of AAR has been reported in dams.

First AAR damage in Turkey was observed during a routine inspection of highway engineers in 1995. Extensive cracks were discovered on the decks, piers and abutments of six highway bridges (Naldöken, Turgutlu, Buca, Hilal2, Halkapınar and Turan) along with other structures which were all built in a period from mid-80s to mid-90s in the vicinity of Izmir (see Figure 1). The deteriorated bridges were investigated as a part of the study on the maintenance and rehabilitation of highway bridges in the republic of Turkey in which Oriental Consultants Co. Ltd. and Japan Overseas Consultants Co. Ltd. and Turkish General Directorate of Highways (KGM), funded by the Japan International Cooperation Agency (JICA). The findings of this study were reported by Tetsuya Katayama, who was chartered by JICA, for KGM engineers in Ankara, Istanbul and Antalya in May, 1996 [2], and were later published as the first international documentation on the occurrence of AAR in Turkey [3]. It was stated that the local sand-gravel particles from Gediz and Nif river systems containing more than 3% reactive glassy rhyolite were the cause of deleterious ASR expansions of several concrete bridges in the Izmir area.

Today, most of the ready-mixed concrete producers use the abundant sources of crushed fine and coarse non-reactive limestone aggregate nearby Izmir, as suggested by the above reports. This, in fact, is more economical than transporting the aggregate from the river basins around the city.

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Until the discovery of the problem, TS 2517 which is similar to ASTM C289 was adopted as a screening test for reactive aggregates. However, this method was not suitable for detecting the reactivity of Turkish aggregates. Afterwards, the general approach has become to conduct accelerated mortar bar tests (ASTM C1260 or similar) to detect the reactivity of the aggregates. If found to be deleterious, the suspicious aggregates are mixed with a known non-reactive aggregate and/or mineral admixtures (generally fly ash or natural pozzolans) are incorporated, and again tested by accelerated mortar bar test.

In the beginning of 2000s, utilization of local mineral admixtures in concrete mixtures containing local reactive aggregates was studied by many researchers [4-6] and the documentation of deterioration has been continued [7]. Many other aggregate sources in the country were also found to be reactive; including Bozdivlit basaltoids from Aliaga [8], basalts from Nigde [9], sand and gravel from Koc River [10], sand from Firat (Euphrates) River [11], cherts from Ankara [12] and sand/gravel from Sakarya [13] as represented in Figure 2 [14],

Reported ASR expansions are investigated by some test methods, e.g., accelerated mortar bar test, concrete prism test and concrete microbar test [15-16]. The effect of gradation and the size of the particles on ASR expansions were also evaluated [17]. These studies revealed that crushing the aggregate may alter the expansion properties of aggregate due to changing microstructure. Microbar test, by some modifications, is an accelerated method which permits to investigate alkali silica reactivity of both fine and coarse aggregate separately or together in a mixture.

An interesting research on alkali aggregate reaction is the rehabilitation studies of the aggregate used in the construction of Deriner Dam [18]. The dam is being constructed in the north-eastern part of Turkey on Coruh River and will be the highest dam in Turkey and fifth highest dam in the world with its height being 252 m from the base when completed. The amount of concrete to be cast until the planned project period - 2012- will be about 4×10^6 m³. Two types of aggregate samples having 20% and 30% of reactive silica are tested in accordance with ASTM C1260 and their 14 day expansions were recorded as 0.115% and 0.157%, respectively. The expansions were reduced to safe levels with the utilization of 25% to 35% of fly ash.

2 ADDITIONAL STUDY ON DETERIORATED HIGHWAY BRIDGES

Katayama's study [3] on the deteriorated highway bridges includes accelerated core expansion tests from the concrete of five deteriorated bridges, EPMA (EDS) analyses of unhydrated cement particles from these cores to estimate minimum alkali content of cement used, and accelerated mortar bar test (CSA A23.2-25A, similar to ASTM C1260) of questionable aggregate sources. It was found that the local sand-gravel particles from Gediz and Nif river systems containing more than 3% reactive glassy rhyolite were the cause of deleterious ASR expansions of several concrete bridges in Izmir area. He reported at the 11th ICAAR in 2000 that glassy rhyolite abounds in cristobalite, suggestive of having a pessimum proportion [3].

2.1 Compositional Trends of ASR Gel and Alkali-Budgets in Concrete

A glassy rhyolite particle with a milky white tint, rich in cristobalite due to incipient devitrification as indicated by XRD analysis, popped out 1 week after coring (Figures.3 a,b,c). This resembles in appearance and mineralogy Whakamaru rhyolite in New Zealand with a marked pessimum proportion of 10%. A siliceous limestone developed conspicuous reaction rim and radial expansion cracks (Figures.3 d,e) coming from siliceous fossils now being replaced by ASR gel (Figure.3f). Active ASR gel separates alkali-rich ASR sol during storage, leaving siliceous ASR gel [19]. Recently, ASR gel in the polished thin sections from the deteriorated concrete (Hilal-2), stored for 11 years (30mm by 20mm, thickness 15 μ m), were analysed by EDS in Japan (JEOL JED2140, 15kV, 0.12nA, data acquisition time 100s, dead time 35%). Compositional trends of such residual ASR gel in the reacted rhyolite and limestone particles are shown in Table 1 and Figures.3g,h.

Alkali-budgets of concrete were estimated to update the published data for the five structures near Izmir [3], based on the minimum cement alkali by EDS analysis of unhydrated cement particles, water-soluble alkali of bulk concrete, and fine aggregates and cements obtained in 1995-96 (Table2). Two important factors, i.e. the ratio of water-soluble alkali (0.5) and of minimum cement alkali (1.2) over the total cement alkali that includes soluble alkali sulphates, came from the analysis of the ordinary Portland cement. Thus, estimated total alkali of cement and concrete ranged Na₂O_{eq} 2.4-3.3kg/m³ and 2.5-4.0 kg/m³, respectively, in which 0.3-

0.7 kg/m³ were contributed from the coarse aggregate and chemical admixture used, although one structure should have a smaller conversion factor.

3 A CASE STUDY FROM ADNAN MENDERES AIRPORT, IZMIR

The deteriorated apron and taxiway concrete pavements of Adnan Menderes Airport (ADB) (38°17'21"N 27°09'18"E) located in Izmir, Turkey were investigated. The deteriorated apron and taxiways were built in 1985 as an addition to other existing airport structures. During this construction, it was stated by the authorities that the concrete was produced by using the same aggregate sources as that were used in the deteriorated highway bridges. Approximately five years after the construction of above-mentioned parts, the operation engineers observed a closing of construction joints and cracking. Until 2004, the signs of deterioration have increased while concrete continued expanding, thus, a renovation has become a necessity. Site observations revealed extensive map-cracking and moving joints while the old apron and other airport buildings showed no sign of deterioration. The photographs shown in Figures 4. a,b were taken during the main author's site visit just before the renovation in 2004.

In 2004, the cracked pavements were demolished and then they were rebuilt by using the local crushed limestone. Operation engineers state that they observed no sign of deterioration on the newly build structures during seven years period. The problem with ASR in Izmir region was substantially decreased after the first studies in the late 90s by the crushed limestone aggregate sources replacing the reactive sources and by increasing utilization of blended cements. However, the maintenance of available massive structures built in 80s is still under consideration.

In order to investigate this case in more detail and to put forward the cause of deterioration, concrete petrography was applied recently. Pristine and polished sections were analysed by optical microscopy, and their thin sections by scanning electron microscopy (SEM). This revealed the presence of reacted chert and rhyolite sand particles, abundant ASR gel around the aggregates, and in cracks and in voids. Ettringite was found around the aggregates and in voids. Regarding the environmental conditions of the region, the possibility of an external sulphate attack and freeze-thaw attack (related de-icing salt attack) was minimal.

3.1 Petrographic Examination Methods

From the ADB apron, a 100mm dia. core was extracted for characterization. The core was sawn into two pieces: one was used for thin and polished section preparations, while the other was completely epoxy impregnated and polished for general examination. During the preparation of thin sections, all the cutting, grinding and polishing processes were applied by using laboratory-grade ethanol as the coolant/lubricant liquid, although non-polar solvent is generally desirable to avoid the leaching of alkalis Na and K from ASR gel and deterioration of epoxy bonding. Before thin sectioning, small cuts of concrete specimens were impregnated with low-viscosity epoxy mixed with 1 wt% Hudson-yellow pigment (Figures 4.c,d).

Both standard thin sections with a cover glass and polished-thin sections for electron microscopy for detailed characterization were produced (PELCON automatic thin section machine). A common practice was applied to the grinding (#320 and #1200 SiC grinding papers), polishing (6µm, 3µm, 1µm and ¼µm diamond paste), and cleaning (10s ultrasonic bath in ethanol) to minimize the dropping out of mineral particles. For the transmitted light polarizing microscopy a Leica DMEP petrographic microscope equipped with polarization accessories and semi-apochromat fluorite objectives were used. An environmental electron microscope equipped with energy dispersive spectrometer (Philips XL30, EDS: 15kV, 0.8 nA, detector SUTW type, take-off angle 35.3°, data acquisition time 100 Lsec) was used for qualitative analysis under a high vacuum condition. Polished specimens were carbon coated (Leica EM CED030, thickness 10nm), with the same thickness as the coating of mineral standards for microanalysis (ASTIMEX Scientific Ltd).

3.2 Petrographic Investigation Results of ADB Concrete

Microstructure of thin and polished concrete sections was studied by polarizing microscopy, scanning electron microscopy and EDS microanalysis of ASR gel. Optical photomicrographs of the ADB concrete are given in Figures 4.e-h and SEM photomicrographs are given in Figures 5.a-c. Coarse aggregate was mainly composed of crushed limestone. Fine aggregate contained dominantly (>50%) quartzite and its fragments some of which may be potentially late-expansive. The remaining sand grains were essentially composed of

chert, alkali feldspar/plagioclase fragments, glassy rhyolite and weathered rock fragments. Photomicrographs illustrate reaction of sand particles, i.e. ASR gel exuded along cracks from the glassy rhyolite into cement paste (Figures 4f,g). Cracks in concrete presented a random network, originating from the reacted particles to pass by the surface of inert limestone (Figure 4h) and quartzite particles (Figure 5b), being filled with ASR gel. A typical qualitative EDS analysis of the ASR gel in the air void indicates that the gel was mainly composed of Si and Ca with minor amounts of alkalis Na and K, as shown by the spectrum of ASR gel in Figure 5.d.

The examined parts of the concrete did not seem to show any entrained air characteristics, although measured air content amounted more than 5% (Table 3). Available air voids and some cracks at the interfacial transition zones (ITZ) around the aggregate were significantly filled or lined with ettringite and portlandite (Figure 5.a). Since there is no information related back to the mix design of the airfield concrete structures built in 1985, it was decided to estimate concrete mix design based on the code of practice for the petrographic examination of concrete proposed by the Applied Petrography Group [20] and the references therein. As a result of the petrographic examination of thin and polished sections of the concrete, characteristic information on the concrete mix was obtained as shown in Table 3. The estimated W/C ratio of the concrete was between 0.48 and 0.50, while the cement content was found to be 250 kg/m³.

4 DISCUSSION

In Turkey, the first reported cases of AAR were observed in the structures that were built between mid-80s to mid-90s in the vicinity of Izmir. As a result of the conversion of cement kilns from wet system to dry system, the alkalinity of cement produced in Turkey was raised significantly during this period. Moreover, the sand used in the production of the affected structures was brought from Gediz and/or Nif river beds containing alkali reactive minerals in pessimum portion. Crushed limestone aggregates used in these structures were found to be non-reactive by accelerated mortar bar test [3]. All the examined deteriorated concretes contained crushed limestone coarse aggregate, and the sources of sand-gravel aggregates were widespread. Gravel-sized aggregate particles were sporadically found in the deteriorated bridges, while they were absent from the deteriorated airport pavements. Crushed limestone sand aggregate was also used in some of the deteriorated bridge concretes. It is interesting to note that chert particles in the sand had reacted in the airport concrete, however, this rock type had not reacted significantly in the bridge concretes at the time of examination in 1995.

There has been little knowledge about the mix proportions and/or the amount of reactive constituents of deteriorated concrete. Thus, petrographic methods were used here to estimate these, which gave reasonable estimation for the airport apron concrete: the apparent w/c ratio between 0.48 and 0.50; cement content of 250 kg/m³, and fine aggregate content of 934 kg/m³. The alkali level of cements produced in 2011 (CEM I 42.5) has been unchanged at least since 1996 when the first AAR study was made (0.81-0.97%, PC 32.5), due to the raw materials used. Hence, the alkali budgets of deteriorated bridges was estimated based on EDS analysis of cement particles, water-soluble alkali of bulk structure and unused fine aggregates with the assumption that 300 kg/m³ cement and 850kg/m³ fine aggregate used in the concrete mix. As a result, the estimated total alkali content of the cement and concrete ranged Na₂O_{eq} 2.4-3.3kg/m³ and 2.5-4.0 kg/m³, respectively, in which 0.3-0.7 kg/m³ were attributable to the coarse aggregate and chemical admixture. Thus, the total alkali content of concrete was high enough to cause ASR in concrete, favouring ASR of highly reactive glassy rhyolite with pessimum-causing cristobalite contained in the sand aggregates.

Typical ASR gel formation was observed in the deteriorated bridge and apron concretes. With the concrete from the affected bridges, active ASR gel separated alkali-rich ASR sol, leaving siliceous ASR gel during long-term storage, even on the thin section. Such residual ASR gel in the reacted rhyolite and siliceous limestone (Hilal-2) presented an increase in the CaO content with decreasing alkali content.

Regarding the environmental conditions of the region, the possibility of an external sulphate attack and freeze-thaw attack (related de-icing salt attack) was minimal. During the microstructural examination of ADB apron concrete, ettringite was observed inside the air voids and the cracks around the aggregate presumably created by ASR. Secondary ettringite formation is most probably related to ASR which is similar to cases previously reported in the literature [21, 22], but DEF in the cast-in-place concrete is likely related to the

adiabatic temperature rise in the mass concrete, like dam (e.g.[23]). Hence, this case might be due to over dosage of chemical admixtures, because ready mixed concrete with a small w/c and low slump, typical of the pavement, needs water-reducing agents, which could be an alkali-bearing sulfonic acid material like the type that had been used until mid-80s in Japan (concentration reached Na₂O_{eq} 14% when no agitation was done).

Among the test methods for determining the reactivity of aggregates, the chemical method (similar to ASTM C289) used as standard method in the 1980s and 90s was found to be unreliable for Turkish reactive aggregates. Today, both the mortar and concrete expansion tests are used to evaluate the reactivity of aggregates. A reliable performance test method is needed to be adapted as local specifications in Turkey.

5 CONCLUSIONS

Petrographic techniques enable it to analyse ASR gel, alkali content of unhydrated cement particles, concrete textures to estimate the mix design and alkali budgets of concrete that was cast even more than twenty years ago. In Turkey, the first cases of ASR deterioration manifested itself in a region that the natural sand containing alkali reactive minerals in a pessimum proportion was used in concrete and in a period of time that the cement alkalinity levels increased due to the cement production methods. Moreover, the conventional test methods used in those days were not reliable enough to detect the reactivity of aggregates. Thus, this literature review and microstructural analysis of affected concrete structures presented here revealed the importance of the choice of concrete constituents and test methods to characterise them.

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8 TABLES AND FIGURES

TABLE 1: Residual silica-rich ASR gel after separating alkali-rich sol on reacted aggregates in concrete (Hilal-2 bridge)

Rock type	position	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	SO ₃	Total
Glassy thylolite	in aggregate	72.31	0.00	0.06	0.00	0.41	1.16	9.27	0.00	83.20
	in paste	79.82	0.03	0.23	0.00	0.26	1.18	4.95	0.00	86.47
Limestone	in aggregate	52.10	0.19	0.11	0.00	15.64	1.61	9.82	0.32	79.80

TABLE 2: Alkali-budgets in ASR-affected concrete structures near Izmir

Struc Ture	Clinker			Cement			Concrete				Local fine aggregate		Others
	Minimum alkali by EDS			Total alkali	Water-sol.alk	Water-soluble alkali			Total alkali	Water soluble alkali		Total alkali	
	Measured			estimated	measured				est	measured		est	
	%			Na ₂ Oeq kg/m ³	%				Na ₂ Oeq kg/m ³	%		Na ₂ Oeq kg/m ³	
	Na ₂ O	K ₂ O	(1)	(2)	(3)	Na ₂ O	K ₂ O	(4)	(5)	Na ₂ O	K ₂ O	(6)	(7)
1*	0.49	0.54	0.85	3.06	1.53	0.079	0.041	2.43	3.96			0.24	0.66
2*	0.40	0.81	0.93	3.34	1.67	0.076	0.041	2.34	4.01			0.24	0.43
3	0.43	0.35	0.66	2.38	1.19	0.039	0.030	1.35	2.50	0.019	0.014	0.24	-0.08
4	0.47	0.65	0.89	3.20	1.60	0.063	0.047	2.16	3.76	0.019	0.018	0.26	0.30
5	0.42	0.49	0.73	2.63	1.31	0.070	0.042	2.25	3.57			0.24	0.70
average			0.81										
Cement	Cement			Cement			Concrete				Local fine aggregate		Others
	Total alkali			Total alkali	Water-soluble alkali	Water-soluble alkali			Total alkali	Water soluble alkali		Total alkali	
	measured			estimated	measured				ratio				
	%			Na ₂ Oeq kg/m ³	%				ratio				
	Na ₂ O	K ₂ O	(8)	(11)	(12)	Na ₂ O	K ₂ O	(9)	(10)				
1	0.43	0.82	0.97	2.91	1.43	0.116	0.537	0.47	0.49				
2	0.29	0.79	0.81	2.43	1.19	0.065	0.504	0.40	0.49				

1 Naldöken, 2 Turgutlu, 3 Buca, 4 Hilal-2, 5 Turan; Cement obtained in 1996: 1 OPC (Be), 2 blended cement (Ce)
 (1)(8)(9): Na₂Oeq=Na₂O+0.658K₂O, * Concrete core samples were in small quantities subject to analytical errors
 (2): 1.2 x ((1)/100) x 300 kg/m³; conversion factor 1.2 = 1.3 (total alkali/min alkali) x 0.97 (dilution by gypsum) x 0.96 (dilution by additives), also 1.2 = total alkali of OPC (8)/average of (1) = 0.97/0.81
 (3): 0.5 x (2), 0.5= water-soluble alkali ratio; (4): as 2300 kg/m³, (4) = (3) + (6) + (7);
 (5): Total available alkali of concrete = total cement alkali (2) + water soluble alkali of fine aggregate (6) + water soluble alkali from others (7), including coarse aggregate and chemical admixture, etc. = (2) + (4) - (3)
 (6): Water-soluble alkali of fine aggregate, as 850 kg/m³. For Hilal-2, sand from Gediz river; for others, sand from Nif terrace
 (7): Water-soluble alkali of coarse aggregate and chemical admixture = (4) - (3) - (6)
 Total available alkali from coarse and fine aggregates plus chemical admixture = (6) + (7) = (4) - (3)
 (10): Water-soluble alkali ratio ((9)/(8)); (12): Water-soluble alkali ((9)/100) x 300 kg/m³

TABLE 3: Estimated Mix Parameters of ADB apron concrete			
Mix Parameters			Values
Petro-graphic	Air Void Content	%	5.9
	D max	mm	32
	W/C (apparent)		0.48-0.50
	Paste Volume	%	20.2
	Coarse Aggregate Volume	%	44
	Fine Aggregate Volume	%	35.8
Assump-tion	Coarse Aggregate (Crushed limestone) Density	kg/m ³	2600
	Fine Aggregate (Quartzite-rich) Density	kg/m ³	2620
	Cement (OPC) Density	kg/m ³	3140
Estimati-on	Coarse Aggregate Content	kg/m ³	1144
	Fine Aggregate Content	kg/m ³	934
	Cement Content	kg/m ³	250
	Water Content	kg/m ³	122.5



Figure 1: ASR map cracking on the bridges in the vicinity of Izmir



Figure 2: Representation of reactive aggregate sources on the map of Turkey [14]

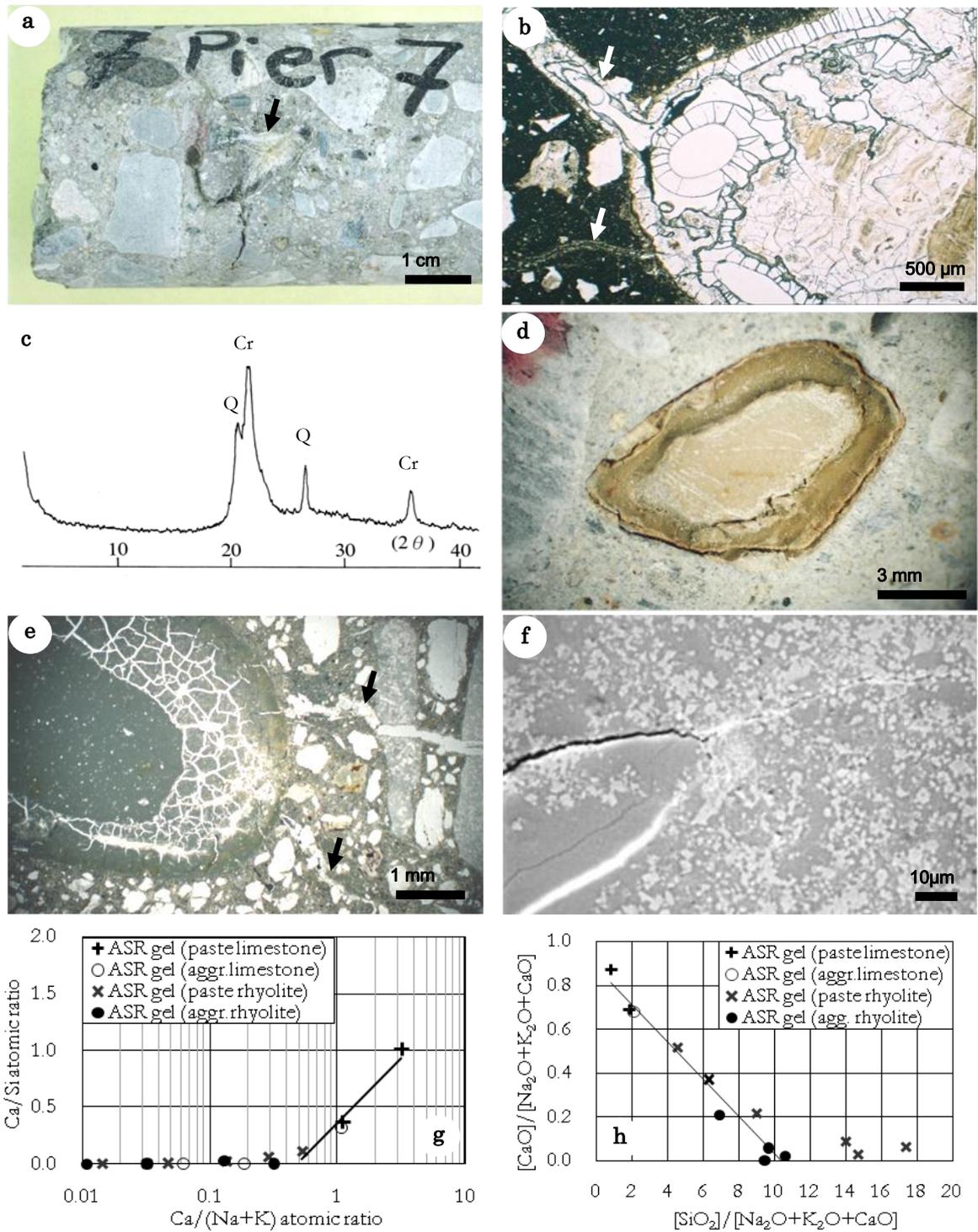


Figure 3: ASR gel in Hilal-2 bridge, Izmir: a) pop-out 1 week after coring, b) on glassy rhyolite particle c) rich in cristobalite. d) Rimmed limestone particle with e) radiating expansion cracks, originated from siliceous fossils now being replaced by ASR gel. g),h) compositions of residual ASR gel after separating alkali-rich sol during storage.

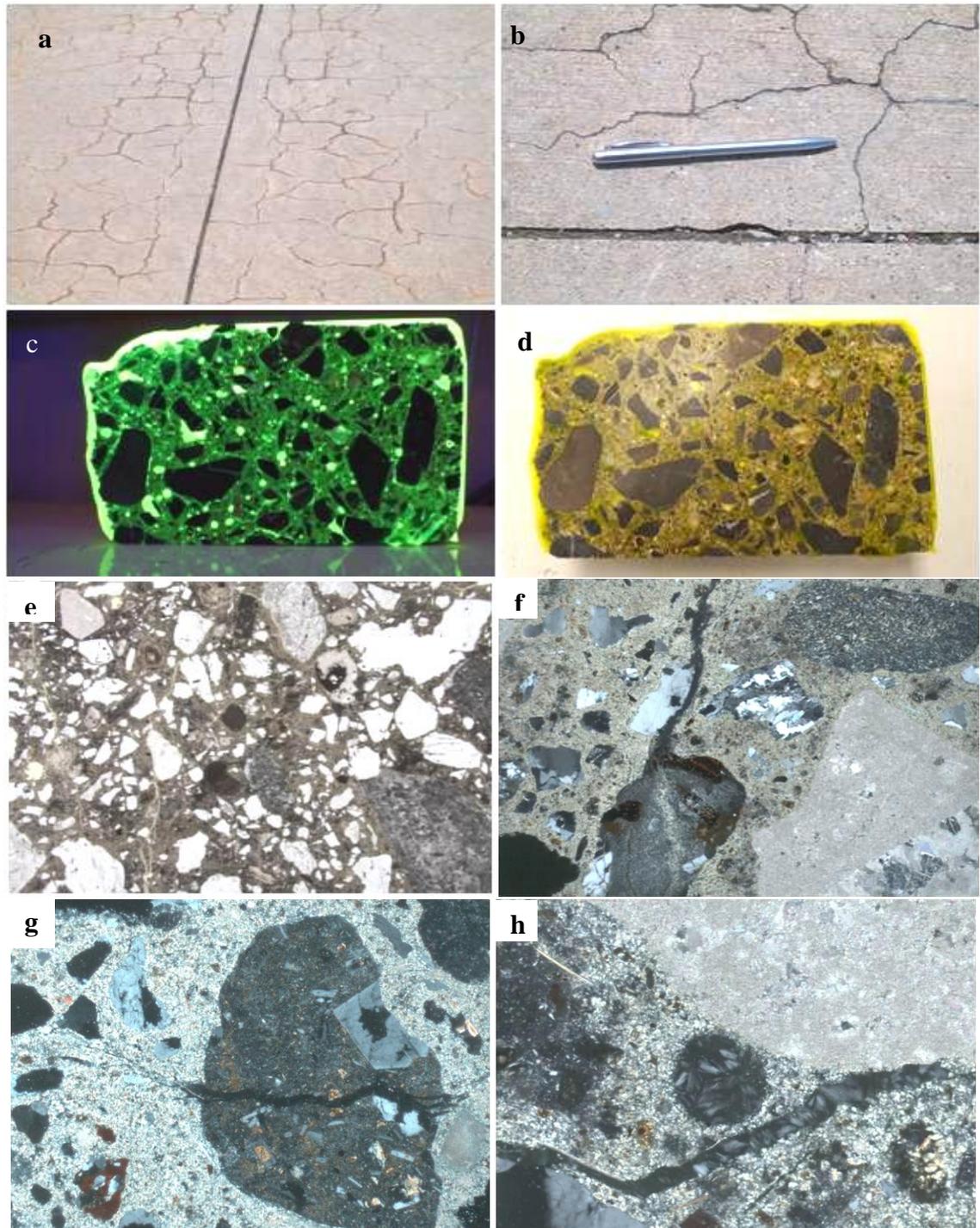


Figure 4: a,b) ASR map cracking observed at ADB apron and taxiways, c),d) Epoxy impregnated polished sections from ADB apron concrete, e)-h) Optical photomicrographs of the ADB concrete. e) Very wide field of view [\leftrightarrow 11.5mm]. PPL image, f) A typical ASR crack formed by a glassy rhyolite sand particle. XPL image, Field of view [\leftrightarrow 2.87mm], g) ASR gel exuding along the crack from glassy rhyolite sand particle. XPL image, [\leftrightarrow 2.1mm]. h) Ettringite precipitation within the air voids and cracks that connect and skirt the particles of both coarse and fine aggregates. XPL image, Field of view [\leftrightarrow 0.71mm].

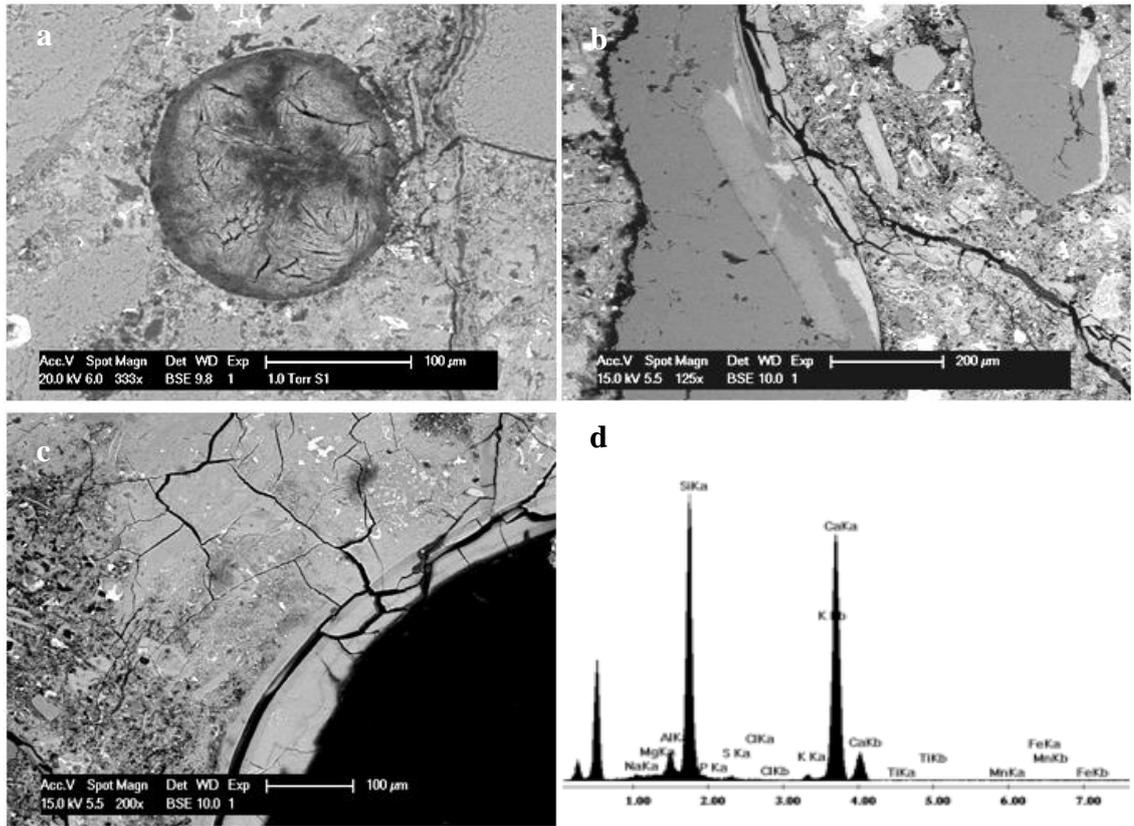


Figure 5: a) Secondary ettringite formation inside air void. b) Crack-filling ASR gel, partly skirting the sand particle of quartzite and extending from other reacted portion in concrete. Note the absence of ASR gel in the grain boundaries of quartz crystals within the inner periphery of this quartzite particle. c) ASR gel migrating into the wall of an air void. d) EDS spectrum of highly Ca-rich ASR gel in the air void.