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## 碱激发材料与普通硅酸盐水泥和混凝土的耐久性能比较

王爱国<sup>a,c</sup>, 郑毅<sup>a</sup>, 张祖华<sup>b,\*</sup>, 刘开伟<sup>a</sup>, 李燕<sup>a</sup>, 石亮<sup>c</sup>, 孙道胜<sup>a,\*</sup>

<sup>a</sup> Anhui Key Laboratory of Advanced Building Materials, Anhui Jianzhu University, Hefei 230022, China

<sup>b</sup> Key Laboratory for Green and Advanced Civil Engineering Materials and Application Technology of Hunan Province, College of Civil Engineering, Hunan University, Changsha 410082, China

<sup>c</sup> Jiangsu Subote New Materials Ltd. Co., Nanjing 211103, China

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### 摘要

中国是世界上普通硅酸盐水泥（OPC）生产量和使用量最大的国家，基础设施建设的快速发展对混凝土材料提出了可持续发展的要求。碱激发材料（AAM）是一种新型节能环保建筑材料，具有广泛的应用前景。本文对比总结了AAM和OPC经硫酸盐侵蚀、酸侵蚀、碳化和氯离子渗透后的耐久性能，阐述了因硅铝质原材料不同和碱激发产物不同，导致AAM耐久性能表现出巨大差异的关系，并根据硅铝质原材料的钙（Ca）含量的高低，对比分析了无钙、低钙、高钙三种体系的AAM的性能劣化机理。尽管目前不同的研究对AAM的耐久性能和长期稳定性存在一定争议，并引起了相当的关注，但总体而言，AAM较OPC表现出了更好的耐久性能。

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## 1. 引言

中国是世界上最大的普通硅酸盐水泥（OPC）生产国和使用国。2018年，中国水泥产量高达 $2.4 \times 10^9$  t，据估算，需要消耗约 $3.0 \times 10^9$  t石灰石、 $7.2 \times 10^8$  t粘土以及 $3.2 \times 10^9$  J能源，同时排放二氧化碳（CO<sub>2</sub>）约 $2.4 \times 10^9$  t。在过去10年里，CO<sub>2</sub>减排目标[1]推动了整个水泥和混凝土行业寻求更绿色环保的生产技术和可替代性胶凝材料。碱激发材料（AAM），又被称为地聚合物，是一类由活性硅铝质原材料与碱性激发剂共同反应形成的胶凝材料[2–4]。目前，关于AAM的反应过程、

聚合机理以及产物的研究已经非常普遍[5–19]。这种在室温或稍高温度（60–80 °C）下进行的反应与制备传统OPC的研磨和煅烧工艺完全不同。因为硅铝质原材料来源广泛，包括工业废渣和副产物，如矿渣（SG）、钢渣、粉煤灰（FA）和热活化粘土[如偏高岭土（MK）]，因而AAM在制备工艺上比OPC更绿色环保，其硬化体具有媲美于OPC的力学性能，并且在大多数侵蚀环境中表现出更好的耐久性能[20]。

碱激发原材料种类繁多，因而不同种类的AAM存在不同的反应机理、产物组成和力学性能。Zhang [21]、Adamiec等[22]、Lothenbach等[23]和Khatib [24]依据硅

\* Corresponding author.

E-mail address: [ZuhuaZhang@hnu.edu.cn](mailto:ZuhuaZhang@hnu.edu.cn) (Z. Zhang), [sundaosheng@163.com](mailto:sundaosheng@163.com) (D. Sun).

铝质原材料中钙 (Ca) 含量的不同将AAM分为无钙、低钙和高钙三个不同体系, 各体系中代表性原料分别为MK、FA和SG (图1)。无钙或低钙体系的产物主要是类沸石 (如方沸石、方钠石等) 凝胶, 而高钙体系的产物则是低钙硅比 (Ca/Si) 的水化硅酸铝钙[C-(A)-S-H]凝胶。目前人们也在尝试使用许多其他硅铝质原材料和工业废弃物作为制备AAM的原材料, 如赤泥、钢渣和煅烧煤矸石。人们也有使用含有潜在活性成分的其他工业废物来制备AAM, 但少量的活性成分可能对AAM的性能, 尤其是耐久性能产生影响[25-27]。

本文综述了近年来学者们对AAM耐久性能的研究进展, 并分别从硫酸盐侵蚀、酸侵蚀、碳化和氯离子( $Cl^-$ ) 渗透四个方面同传统水泥基材料进了对比, 以便更好地了解AAM被用作OPC替代品时应注意的环境条件。本文可为进一步研究不同条件下AAM的开发和应用提供一些参考。

## 2. 硫酸盐侵蚀

硫酸盐侵蚀是影响混凝土耐久性能的重要问题之一, 其破坏机理是一个十分复杂的物理化学反应过程。来自外界环境或混凝土内部 $SO_4^{2-}$ 与水泥水化产物发生了一系列物理化学变化, 导致水泥混凝土出现膨胀、开裂, 并最终使混凝土强度和黏结性能降低甚至丧失[28-32]。目前认为影响混凝土抗硫酸盐侵蚀的主要内因是水泥矿物, 如 $C_3A$ 和 $C_3S$ 的含量以及自身密实度。 $C_3A$ 被认为是生成膨胀性钙矾石的关键因素, 而 $C_3S$ 在水化过程中会生成大量的 $Ca(OH)_2$ , 即CH, 它是形成膨胀性

石膏和钙矾石的因素之一 (图2) [33,34]。硫酸盐侵蚀同样会导致硅酸钙水合物 (C-S-H) 凝胶脱钙, 主要原因是随着石膏的不断形成, CH被不断消耗, 从而引起水泥基材料pH值降低, 较低的pH值环境不利于C-S-H凝胶的稳定存在, 从而引发凝胶结构的脱钙反应。另外, 在碳硫硅钙石型侵蚀中, C-S-H凝胶可作为反应物被逐步消耗, 最终导致混凝土软化、失效[35,36]。

无钙AAM (如MK基AAM) 并不会生成类似于硅酸盐水泥的水化产物[37]。硫酸盐对无钙或低钙AAM的侵蚀是一种离子交换过程, 在此过程中, 硫酸盐溶液中侵蚀性金属阳离子与凝胶组分发生离子交换, 导致孔隙率增加[38]。而高钙AAM [如碱激发矿渣 (AAS)] 的主要产物为C-(A)-S-H凝胶, 其Ca/Si值低于OPC体系中C-S-H凝胶的Ca/Si值[39]。由于反应 (水化) 产物的相似性, 高钙AAM的硫酸盐侵蚀机理与OPC的相似。另

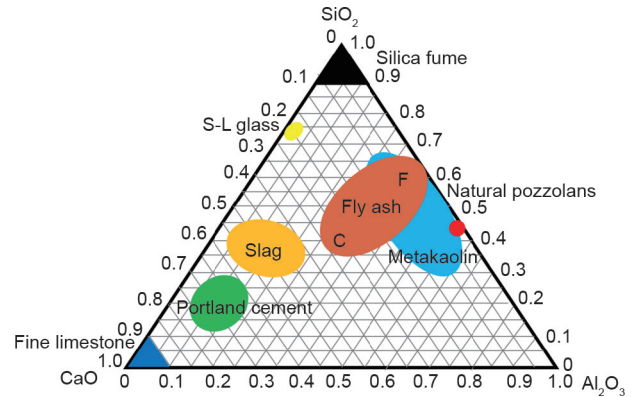


图1. 可用于制备AAM的硅铝质原材料 (MK、FA和SG) 的 $SiO_2$ - $Al_2O_3$ -CaO三元相图。这些原材料与水泥和石灰石的组成特征对比如图所示。经中国颗粒学会和中国科学院过程工程研究所许可, 转载自参考文献[22], ©2008。

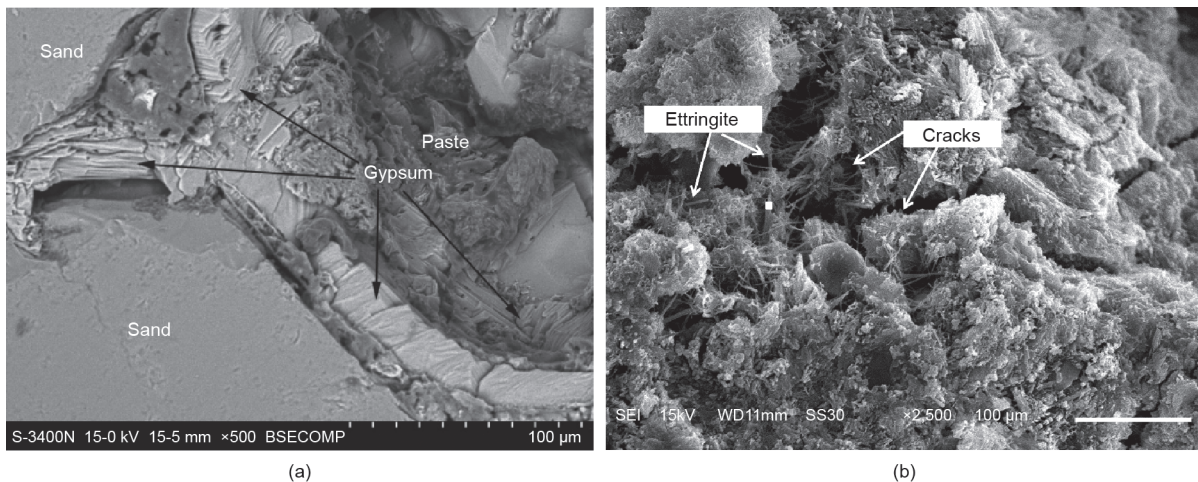


图2.  $Na_2SO_4$ 溶液侵蚀后的OPC砂浆试样的微观结构。(a) 石膏形成;(b) 钙矾石形成。经共同作者KW Liu许可, 转载自参考文献[34], ©2010。

一方面, MK基AAM主要产物是水合铝硅酸钠(N-A-S-H)凝胶, 因此, 其具有不同的抗硫酸盐侵蚀机理。所以, AAM作为OPC抗硫酸盐替代品的设计和使用时应仔细考虑AAM的类型。

Karakoç等[39]研究发现, AAS在硫酸镁溶液中浸泡24周后, 其外观没有发生明显变化, 但抗压强度会随着溶液浓度和浸泡时间的增加而降低。Alcamand等[38]通过在MK基AAM中加入SG和硅灰, 调整硅铝质原料的CaO含量并改变AAM的基体组成(以 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 摩尔比计)。理论上这种结构稳定的AAM应具有较好的抗硫酸盐侵蚀性能。但在硫酸盐侵蚀过程中, (C,N)-A-S-H凝胶中的 $\text{Ca}^{2+}$ 可被外界阳离子交换, 也会引发凝胶结构劣化。因此, Ca的引入对其抗硫酸盐侵蚀性能可能存在一定的负面影响。所以, N-A-S-H凝胶作为低钙或无钙AAM的主要产物, 具有较好的抗硫酸盐侵蚀能力(图3)。相比之下, C-(A)-S-H凝胶作为高钙AAM的主要产物, 容易生成石膏和(或)钙矾石, 从而导致其抗硫酸盐侵蚀性能不佳[38,40,41]。

在AAM耐久性能研究初期, 学者们通过对AAM产物结构的归纳分析, 认为无钙AAM在水化过程中不会

产生钙矾石等硫酸盐矿物, 避免了钙矾石和石膏型硫酸盐侵蚀, 因而无钙或低钙AAM具有更好的抗硫酸盐侵蚀性能[37,42–48]。Tao等[49]通过测定强度变化表征了AAM的抗硫酸盐侵蚀性能, 结果显示, MK基AAM在 $\text{Na}_2\text{SO}_4$ 溶液中浸泡28 d后的强度保持率远高于OPC。Hou等[50]发现, FA基AAM在不同硫酸盐溶液中浸泡150 d后, 抗压强度和表观密度发生显著变化, 并认为硫酸盐溶液对FA基AAM性能的影响与扩散作用有关。此外, 试样在硫酸盐溶液中的耐久性能与激发剂的阳离子类型、硫酸盐溶液中的阳离子和溶液浓度都有关。

Tang等[51]发现, FA基AAM混凝土和OPC混凝土在硫酸盐侵蚀过程中, 其抗压强度均呈现先降低后上升的趋势, 并且在5%  $\text{Na}_2\text{SO}_4$ 溶液中二者质量变化均较小(图4)。用再生骨料制备的FA基AAM混凝土经5%  $\text{Na}_2\text{SO}_4$ 溶液干-湿循环后无损伤, 反而其抗压强度有所增加[52]。Palomo等[53]和Bakharev [54]也得出类似结论。在探究硫酸盐环境下FA基AAM的性能变化和微观结构演变时, Tang等[55]发现, 所制备的试样在硫酸盐溶液中直到60 d时, 试样表面都没有出现裂纹或剥落现象。结果表明, FA基AAM在硫酸钠环境中不会产生对

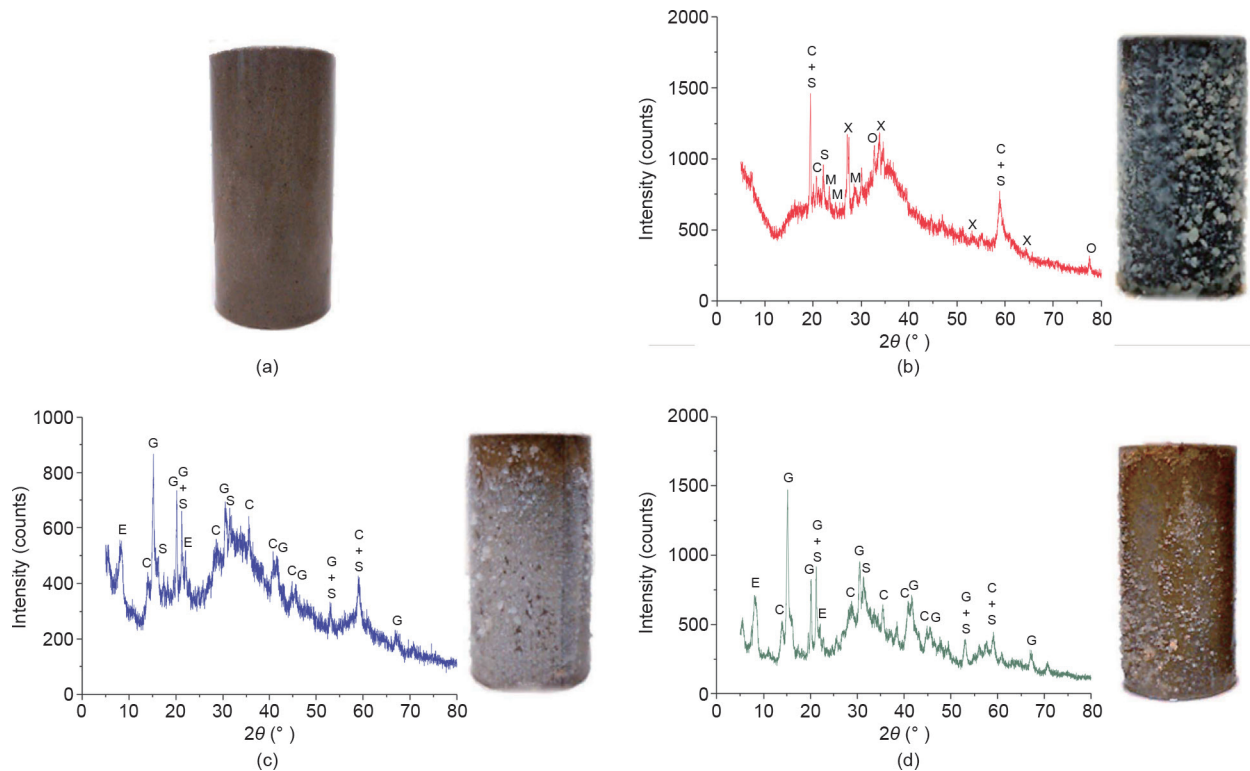


图3. 硫酸镁侵蚀180 d后的AAM样品表面形成的矿物。(a) 以100% MK制备的AAM;(b) 以MK与硅灰比为80/20制备的AAM;(c) 以MK与SG比为80/20制备的AAM;(d) 以MK与SG比为60/40制备的AAM。M: 硫酸镁; C: 碳酸钠; X: 硅酸钠; S: 硫酸钠; O: 二氧化硅; E: 钙矾石; G: 石膏。经Elsevier Ltd.和Techna Group S.r.l.许可, 转载自参考文献[38], ©2018。

结构有害的膨胀产物。

Džunuzovic等[56]分析了 $\text{Na}_2\text{SO}_4$ 溶液与FA-SG基AAM相互作用后的组成变化(表1)。结果发现,溶液中的Si可能来自AAM自身未反应的碱性激发剂组分或凝胶结构中的富硅组分,而侵蚀溶液中Ca浓度的增加则说明,相较于N-A-S-H凝胶,含钙化合物如C-S-H凝胶和C-(A)-S-H凝胶确实存在与腐蚀介质的阳离子交换。Ismail等[57]指出AAM砂浆中Ca的溶出可能与侵蚀溶液的 $\text{Na}_2\text{SO}_4$ 反应或者离子交换有关。Zheng等[58]研究了干湿循环条件下AAM砂浆和水泥砂浆的抗 $\text{Na}_2\text{SO}_4$ 侵蚀性能。结果表明,经75次循环后,AAM砂浆的抗压强度系数优于OPC砂浆。AAM砂浆的腐蚀产物只有硫酸钠相。

Elyamany等[59]发现随着养护温度的升高和激发剂摩尔浓度的增加,FA基AAM的吸水率和孔隙率在降低,从而提高了其抗 $\text{MgSO}_4$ 侵蚀性能。然而,在被 $\text{MgSO}_4$ 侵蚀后的AAM样品中发现了石膏晶体,侵蚀后出现的微裂纹可归因于石膏相的生成。Jin等[60]发现,浸泡在5%  $\text{MgSO}_4$ 溶液中的FA基AAM试样的抗压强度先降低后升高,说明 $\text{Mg}^{2+}$ 在AAM混凝土中的扩散和碱金属离子在溶液中的迁移同时发生。可以推断,经过长时间双向离子的扩散和迁移,这两个过程最终会达到相

对平衡状态。这一证据表明,AAM的Ca含量和硫酸盐类型(如钠盐或镁盐)是影响其抗硫酸盐侵蚀性能的两个关键因素。

综上所述,无论是OPC还是AAM,硫酸盐侵蚀都是一个动态发展的过程。侵蚀机理取决于水化产物的性质。OPC在遭遇硫酸盐侵蚀的时候主要发生了一系列复杂的物理化学反应,这些化学反应和物理影响会生成额外的晶体和内应力。水泥混凝土的软化通常是由C-S-H凝胶的脱钙劣化导致的,而结构的膨胀和开裂则是由于石膏和钙矾石的形成[61]。高钙AAM的主要产物为C-(A)-S-H凝胶,硫酸盐侵蚀机理与OPC的类似。然而对于无钙或低钙AAM,硫酸盐溶液与AAM之间发生了离子交换反应。在侵蚀过程中,N-A-S-H凝胶的网络结构的孔隙不断变化并逐渐形成微裂纹,最终导致AAM结构劣化。

### 3. 酸侵蚀

OPC水泥和混凝土具有较高的pH值和多孔特性,且耐酸侵蚀性能比较差。酸性物质与水泥混凝土中的CH和C-S-H凝胶反应,形成无胶凝性产物或水溶性物质,导致混凝土破坏。酸性物质还促使水化硅酸钙和水

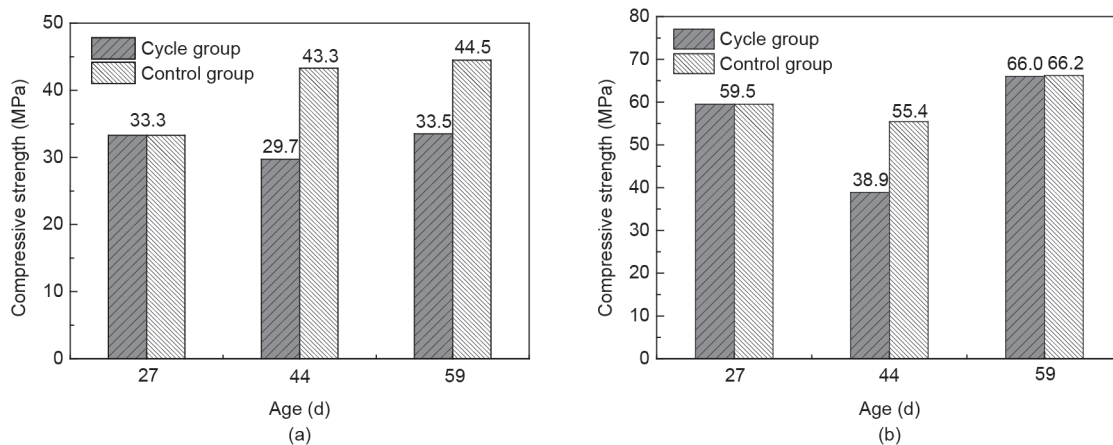


图4. OPC混凝土(a)和FA基AAM混凝土(b)在5%  $\text{Na}_2\text{SO}_4$ 溶液中浸泡27~59 d后的抗压强度。经《材料导报》许可,转载自参考文献[51], ©2015。

表1 5%  $\text{Na}_2\text{SO}_4$ 溶液与碱激发FA-SG材料相互作用前后的pH值及组成分析[56]

Time (d)	pH	Ion concentration in $\text{Na}_2\text{SO}_4$ solution ( $\text{mg}\cdot\text{L}^{-1}$ )				
		Na	Si	Ca	Al	Mg
0	6.04	14 140	6	5.4	0.7	0.9
30	13.11	14 760	143	31.4	2.4	0.9
90	11.30	17 880	52	73.6	0.5	0.9
180	11.25	16 880	32	71.2	0.8	0.9

化铝酸钙的分解,从而破坏胶凝体,使混凝土强度降低[62]。Wang等[63]发现,在酸性溶液(pH=2)中浸泡的混凝土,其表面首先形成一层白色黏性物质,然后变软。Ning等[64]发现,酸侵蚀首先从试样的表层开始,其侵蚀程度与溶液pH值成反比。Alexander[65]分析认为,水泥基材料在酸侵蚀过程中,表层结构中的CH首先会与酸反应,从而增大孔隙率,加速了内部结构的酸侵蚀。当孔隙溶液的pH值降至12.4以下时,C-S-H凝胶脱钙,并伴随着 $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$ (AFm)和 $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-tri}$ (Aft)的溶解。

AAM通常表现出比OPC更好的耐酸侵蚀性能[66–68]。表2总结了部分学者近年来关于不同类型酸侵蚀AAM的研究工作[68–75]。高钙AAM在酸侵蚀过程中凝胶结构也会发生脱钙反应,但由于一些AAM的渗透性比OPC低,所以这一过程要慢得多。另外,铝硅酸盐凝胶的致密层可阻止酸性物质的进一步侵蚀[76,77]。

Bouguermouh等[72]认为,影响AAM耐酸侵蚀性能的主要因素是硅铝质原材料的矿物组成和激发剂中碱金属阳离子的种类。酸侵蚀( $0.1\text{ mol}\cdot\text{L}^{-1}\text{ HCl}$ )对于MK基AAM产物中的N-A-S-H凝胶仅有轻微的影响,除了部分酸侵蚀导致凝胶层出现由收缩导致的细微裂缝外,基体材料仍然能够保持较好的层状结构。Jin等[78]发现,MK基AAM在酸雨侵蚀循环试验中( $\text{SO}_4^{2-}/\text{NO}_3^-$ 摩尔比=3/4),其外观几乎没有受到影响。另外,X射线衍射(XRD)分析表明,其主要矿物成分没有明显变化。

Zheng等[79]将FA基AAM浸泡在5%硫酸( $\text{H}_2\text{SO}_4$ )溶液中,28 d后发现,该试样仍然能满足《建筑防腐蚀

工程施工及验收规范(GB 50212—2002)》中的浸酸安全指标。Zhao等[80]认为N-A-S-H凝胶作为FA基AAM的主要产物,具有良好的耐盐酸侵蚀性能,且凝胶结构受酸的侵蚀影响较小。当FA中的Ca含量较高或酸的类型改变时,耐酸性可能会降低。Mehta和Siddique[81]发现,硫酸在侵蚀FA基AAM过程中,除了 $\text{H}^+$ 会与基体材料发生反应, $\text{H}_2\text{SO}_4$ 中的 $\text{SO}_4^{2-}$ 同样会与产物中的 $\text{Ca}^{2+}$ 结合生成 $\text{CaSO}_4$ (图5)。这两种侵蚀过程的相互作用加剧了试样的劣化。

AAM和OPC都是碱性材料,需要在一定碱度条件下才能保持稳定,它们在酸侵蚀过程中会不可避免地发生一定程度劣化。由表2可知,由于AAM的固有组成和结构特征,其耐酸侵蚀性能明显优于OPC。Shi和Stegemann[82]以及Beddoe和Schmidt[83]认为,在酸侵蚀过程中,硬化水泥浆体的耐酸侵蚀性能依赖于保护层或水化产物的自身特性,而不是硬化浆体的孔渗透性。Gutberlet等[84]分别探究了pH=2、3和4情况下的水泥基材料的耐酸侵蚀性能并发现,在酸侵蚀过程中,水泥基材料表层会形成高孔隙度、低强度的劣化层。劣化层和未被侵蚀的材料之间的过渡区如图6所示。所形成的表面劣化层以及过渡区是决定材料耐久性性能的关键因素。如果表面劣化层相对致密,可有效地将内部基体材料隔绝保护起来,阻止酸的进一步侵蚀。

## 4. 碳化

混凝土碳化是指空气中酸性气体 $\text{CO}_2$ 与混凝土中液

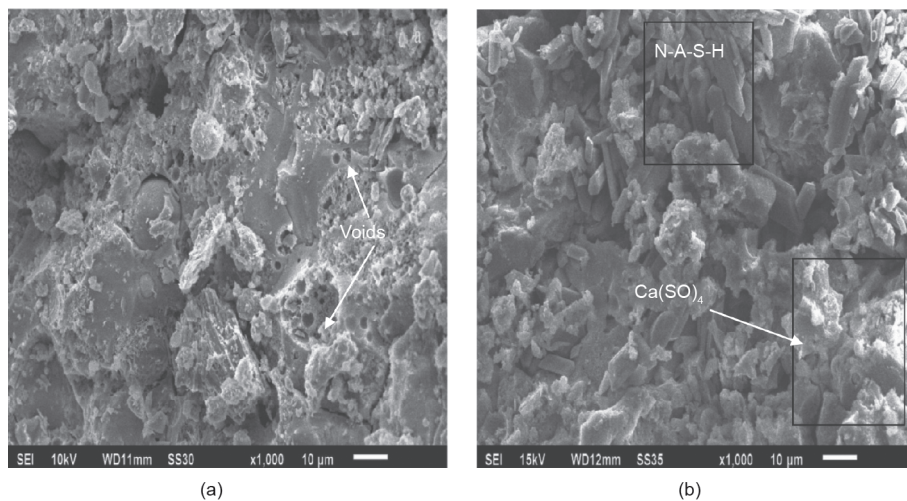


图5. 掺有10% OPC的FA基AAM在5%  $\text{H}_2\text{SO}_4$ 溶液中被酸侵蚀前(a)、后(b)的扫描电子显微镜(SEM)图像。经Elsevier Ltd.许可,转载自参考文献[81], ©2017。

表2 AAM不同种类酸侵蚀的研究工作

AAM (activator)	Experimental conditions	Performance changes	Comments	Refs.
FA	H <sub>2</sub> SO <sub>4</sub> 12 months	Compressive strength decreases by 65%	Acid reacts directly with sample, causing structural degradation	[69]
FA and SG (NaOH + sodium silicate)	H <sub>2</sub> SO <sub>4</sub> (pH = 0.8) 9 months	FA-based: Mass loss is 5.4%. Compressive strength decreases by 10.9% SG-based: Mass loss is 9.6%. Compressive strength decreases by 7.3%	AAMs are more stable than OPC	[70]
FA (NaOH + sodium silicate)	HCl (pH = 1.0) 90 d	Weight loss of 2.5%. Strength decreases by 23%	HCl causes N-A-S-H gel to degrade Al and generate SiO <sub>2</sub> -rich zeolite	[71]
MK (NaOH + sodium silicate/ KOH + potassium silicate)	HCl (pH = 1.47) 28 d	Surface of the sample is slightly degraded and the color is unchanged	Secondary minerals in products can alleviate acid corrosion	[72]
MK (KOH + potassium silicate)	HCl (pH = 2.0) 28 d	Geopolymer structure remains after 28 d of corrosion	K <sup>+</sup> and H <sup>+</sup> undergo ion exchange in the product structure	[73]
SG (sodium silicate)	CH <sub>3</sub> COOH (pH = 4.5) 150 d	Sample strength retention rate is about 75%	Aluminosilicate gel produced by decalcification is small and mechanical strength is higher	[68]
FA (NaOH/KOH + sodium silicate)	CH <sub>3</sub> COOH (pH = 2.4) 6 months	About 40% strength loss	The structure and acid corrosion products of AAM prepared by different activators are different	[74]
SG plus FA (NaOH + sodium silicate)	Organic acid (pH = 3.0) 18 weeks	As the content of Ca decreases, the mass loss of the sample decreases, and the residual compressive strength increases	Corrosion resistance: C-S-H < C-(A)-S-H < N-A-S-H	[75]

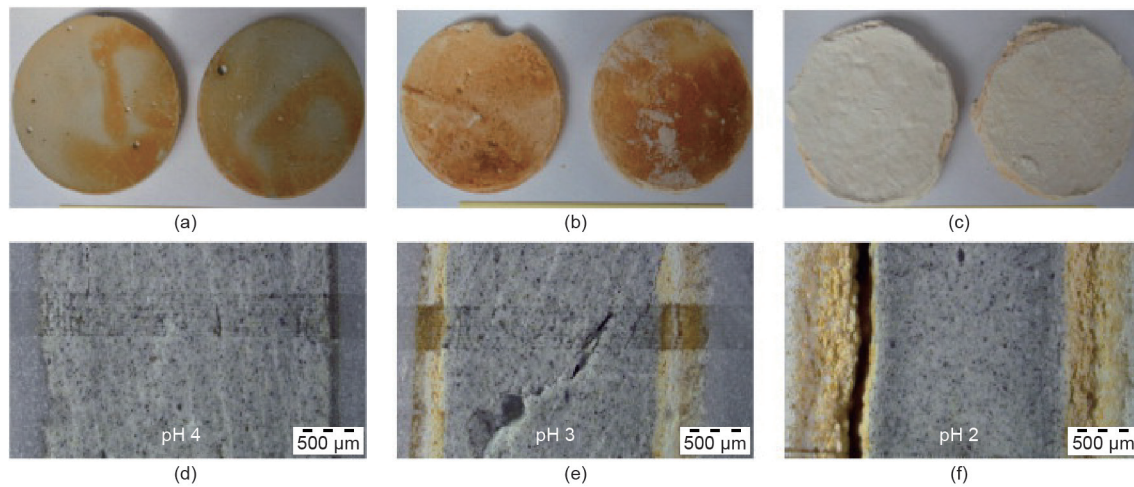


图6. (a)~(c) 在H<sub>2</sub>SO<sub>4</sub>溶液中保存28 d后被侵蚀的OPC样品, pH值从左至右分别为4 (a)、3 (b)和2 (c)。(d)~(c) 相应样品横截面的显微照片。经Elsevier Ltd. 许可, 转载自参考文献[84], ©2015。

相碱性物质发生中性化反应, 使得混凝土碱度下降、成分发生改变[85]。碳化本身对混凝土没有明显的破坏作用, 其主要危害在于, 碳化导致混凝土碱度降低, 使得保护钢筋的钝化膜遭到破坏。在水和空气的共同作用下, 钢筋产生锈蚀, 最终由于内部膨胀应力而使混凝土结构遭到破坏[86]。Shi等[87]指出, 碳化反应会将混凝土的pH值从最初的大于13降到8左右。碳化同样会引起硬化水泥浆体的孔径分布和孔隙率发生变化(由于CH

的碳化产物CaCO<sub>3</sub>总体积大于CH), 进而影响有害离子(如Cl<sup>-</sup>、SO<sub>4</sub><sup>2-</sup>)在混凝土中的扩散。原本排列致密的C-S-H凝胶结构不复存在, 取而代之的是不规则的团簇状C-S-H凝胶结构[88]。碳化过程中, 由于孔隙溶液pH值的降低, 导致硬化水泥浆体中Friedel盐(单氯铝酸钙)的分解, 从而使混凝土孔隙变大及混凝土中Cl<sup>-</sup>的扩散系数升高[89,90]。Papadakis等[91]模拟了水泥基材料的碳化过程, 具体如下: CO<sub>2</sub>首先在水泥基材料孔隙中扩

散，同时水化产物CH在孔隙溶液中溶解，然后溶解于孔隙溶液中的CO<sub>2</sub>与CH反应生成CaCO<sub>3</sub>。通常CH在自然碳化情况下的主要产物为方解石、球霏石和文石[92]。碳化过程往往伴随着微结构的改变，如CaCO<sub>3</sub>的形成、脱钙C-S-H凝胶的聚合以及钙矾石的分解[93]。作为水泥的主要水化产物，C-S-H凝胶和CH极易被碳化[94]。C-S-H凝胶碳化的过程包括C-S-H凝胶的脱钙和无定形凝胶的形成。在整个碳化过程中，产物的总体积减小，孔隙率和孔径增大[95,96]。

AAM的碳化机理不同于传统水泥基材料，并且高钙体系与低钙体系AAM的反应机理也不相同。在高钙AAM的碳化过程中，CO<sub>2</sub>溶解在孔隙溶液中生成的碳酸会直接与C-(A)-S-H凝胶发生反应生成CaCO<sub>3</sub>，而低钙FA基AAM的主要产物N-A-S-H凝胶并没有脱钙过程，其碳化过程主要是孔隙溶液由高碱度向高浓度碳酸钠转变[97,98]。

AAS的主要产物是具有低结晶度和均匀致密的非晶态特征的C-(A)-S-H凝胶。在碳化过程中，由于AAS的产物不包含CH，因此，在碳化过程中，通过C-(A)-S-H凝胶的脱钙作用直接维持Ca<sup>2+</sup>的动态平衡[99]。由于Ca<sup>2+</sup>的脱除，C-(A)-S-H凝胶体积收缩并且聚合度增加。碳化作用进一步将C-(A)-S-H凝胶转化为硅胶，导致了更大的收缩[100]。在自然碳化的过程中，AAS的主要碳化产物是Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O，而在加速碳化条件下，主要碳化产物为NaHCO<sub>3</sub>[101]。Chen等[102,103]发现，在CO<sub>2</sub>浓度为20%的加速碳化的过程中，AAS砂浆的碳化速率高于OPC砂浆。碳化会使砂浆收缩，导致骨料周围产生微裂纹，并会增大浆体的孔隙率和砂浆的CO<sub>2</sub>

扩散系数。Yu等[104]研究了激发剂用量对AAS抗碳化能力的影响并指出，AAS在CO<sub>2</sub>浓度为20%的加速碳化条件下，其抗碳化能力随着硅酸钠用量的增加而提高。Dong等[105]以矿粉和Pisha砂岩为原料制备了AAM，并在加速条件下进行了碳化研究。他们认为，NaOH用量的增加会使抗碳化能力得到增强。

对于低钙AAM，Li等[106]发现，在CO<sub>2</sub>浓度为5%的条件下碳化的FA基AAM结构中的细裂纹数目明显减少，并且FA基AAM的微观结构则变得更为致密（图7）。在整个碳化过程中，孔隙溶液的pH值基本降低至约11。Bernal等[107]提出，FA基AAM的主要产物N-A-S-H凝胶在碳化过程中是稳定的，只有当孔隙溶液中的OH<sup>-</sup>与碳酸反应时，N-A-S-H才会溶解。当加入钙质原料时（如在FA基AAM [106]或在MK基AAM [108]中掺入SG），AAM的抗碳化能力通常会降低。

根据Pouhet和Cry [109]的研究，在CO<sub>2</sub>的自然浓度条件下，无钙AAM的孔隙溶液的碳化反应会随着pH趋于稳定，并被分为两个不同的阶段：在第一阶段，在暴露于CO<sub>2</sub>气氛的前两周内，孔隙溶液基本完全碳化，Na<sub>2</sub>CO<sub>3</sub>形成，pH值达到12左右；在第二阶段，碳酸盐与碳酸氢盐之间发生相平衡的演变，促使碳酸氢盐（在180 d时，浓度为10%）形成，此时pH值约为10.5。孔隙溶液的pH值高于钢的钝化极限值9。MK基AAM的抗压强度则保持不变（图8）。

由此得出结论，AAM的抗碳化能力不如OPC，但其pH值可以保持在10.5以上。然而，依然存在一些争议性研究结果，Huang等[110]报道说，经过CO<sub>2</sub>浓度为20%的碳化试验，OPC的强度有所提高，而FA基AAM

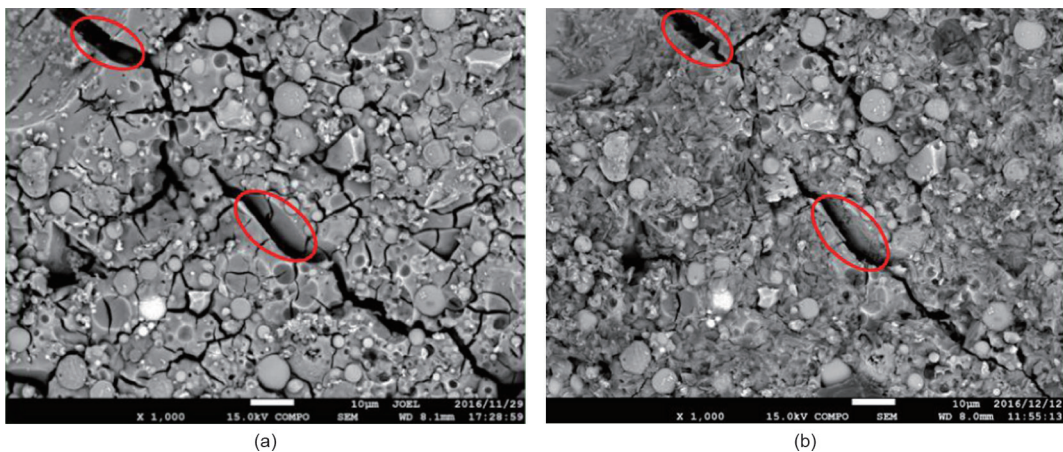


图7. FA基AAM在5% CO<sub>2</sub>浓度下进行碳化试验前（a）、后（b）的SEM图像[106]。经Elsevier Ltd.许可，转载自参考文献[106]，©2018。

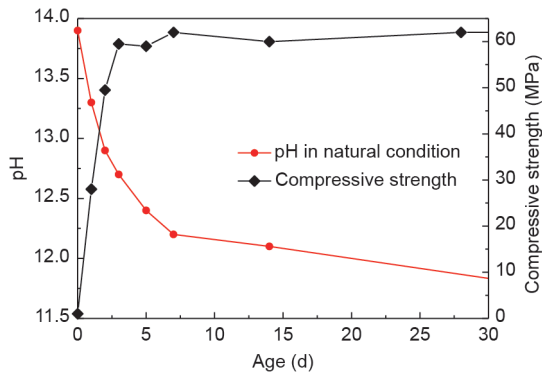


图8. 在自然CO<sub>2</sub>环境下养护的MK基AAM的孔隙溶液的pH值演变及其抗压强度[109]。经Elsevier Ltd.许可，转载自参考文献[109]，©2016。

的强度不受碳化的影响。Badar等[111]制备的FA基AAM则在加速碳化450 d后出现了钢筋锈蚀、pH值显著降低、机械强度性能降低以及总孔隙率增加。

研究表明的AAM抗碳化能力存在明显争议可能与抗碳化性能测量方法的选择有关。Huang等[112]指出，酚酞指示法和pH值不适合作为确定FA基AAM抗碳化能力的有效判据。Yu等[104]指出，该测试方法对AAM的抗碳化性能的测试结果有影响，通过电化学法和钻孔采样法获得的结果比使用酚酞指示法获得的结果的一致性要好。Bernal等[101]指出，AAS通过自然碳化和加速碳化形成的产物不同。CO<sub>2</sub>浓度的增加会直接影响CO<sub>3</sub><sup>2-</sup>和HCO<sub>3</sub><sup>-</sup>的平衡，从而对pH值产生影响。OPC在碳化过程中，孔隙溶液的pH值、矿物组成和孔隙结构也都取决于CO<sub>2</sub>浓度[113]。

此外，用于制备AAM的原材料的特性会影响碳化结果。目前行业内尚无AAM相关标准，只提出了一些建议。例如，FA基AAM需要高浓度的NaOH溶液，并且在60 °C下养护48 h会完成基本的聚合反应[114,115]。原料的物理和化学特性因地制宜，导致AAM的性能和微观结构的差异[116]。Bernal等[117]认为，AAS的微观结构变化在很大程度上取决于SG的化学组成和矿物组成。激发剂的种类和AAS浆体的体积会对抗碳化性能产生很大的影响。此外，AAS多孔结构的含水量会影响碳化试验。研究表明，当OPC孔隙结构的相对湿度(RH)在50%~70%之间变化时，CO<sub>2</sub>扩散速率会提高，而当RH高于70%时，毛细孔被水填充，CO<sub>2</sub>扩散速率降低[118]。原材料、实验条件和结构内部含水量的不同必将导致AAM的抗碳化性能研究结果的不同。

风化是一种与碳化相关的物理化学过程，风化的反应过程类似于无钙或低钙AAM的碳化反应（侵蚀过程

仅消耗游离碱而不会对基体造成损害）过程[119,120]。Kani等[121]指出，当混凝土柱与其底部的潮湿土壤接触时，水通过毛细管作用迁移到混凝土表面并蒸发，可溶性碱被溶解，并与空气中的CO<sub>2</sub>反应，随着水的蒸发最终沉淀在混凝土表面。Pouhet和Cyr [109]指出，风化不会造成胶凝材料真正的耐久性能问题，只会严重影响OPC和AAM的外观。

AAM包含大量可溶性碱（如NaOH和KOH）。Provis等[122]认为，Na<sup>+</sup>在网络结构中不稳定，甚至可以溶解在孔隙溶液中。风化主要由以下原因导致：① AAM的开口孔隙和低密度会导致风化；② 碱性激发剂过量导致孔隙溶液中含有高浓度的碱；③ Na<sup>+</sup>与AAM的网络结构结合能力较差[123–125]。

Zhang等[119,126]认为，影响FA基AAM风化的主要因素包括激发剂的碱含量、激发剂的种类和养护温度。其中激发剂的碱含量是影响风化的最重要因素，FA基AAM内部的游离碱会在部分干燥和潮湿的条件下引起风化（图9）。AAM内部结构中较大的孔径分布以及较高的总孔隙率会导致碱浸出速度加快，从而引起更严重的风化，但试样表面的风化不会改变基体材料的矿物组成。

## 5. 氯离子渗透

Cl<sup>-</sup>渗透是导致混凝土中钢筋锈蚀的主要原因。由于其对混凝土结构破坏作用明显，目前Cl<sup>-</sup>渗透已经成为耐久性能研究的重要内容。在Cl<sup>-</sup>的作用下，钢筋混凝土结构的腐蚀损坏通常表现为钢筋表面锈蚀以及生成膨胀性锈蚀产物导致混凝土覆盖层的开裂和剥落[127]。混凝土中的Cl<sup>-</sup>通常来源于以下两部分，即混凝土内部混合物成分中的Cl<sup>-</sup>和从外部环境渗入的Cl<sup>-</sup>。部分Cl<sup>-</sup>以游离态形式溶解在孔隙溶液中，部分Cl<sup>-</sup>通过化学或物理结合的方式结合在水泥水化产物中[128]。影响Cl<sup>-</sup>渗透的主要因素是硬化水泥浆体的孔隙结构，孔隙结构越粗，孔越开放，渗透性也越大；硬化水泥浆体结合Cl<sup>-</sup>的能力同样影响Cl<sup>-</sup>在混凝土中的渗透性[129,130]。Martín-Pérez等[127]指出，胶凝材料的Cl<sup>-</sup>结合能力对混凝土中Cl<sup>-</sup>的迁移速率和钢筋锈蚀有重要影响。Xie等[130]认为，当游离态的Cl<sup>-</sup>到达钢筋表面并达到一定浓度时，钢筋才会被锈蚀。因为碳化会影响硬化水泥浆体的孔隙结构，碳化和Cl<sup>-</sup>渗透之间有着密切的关系（耦合效应）。Cl<sup>-</sup>在混凝土中的迁移是一个极为复杂的过



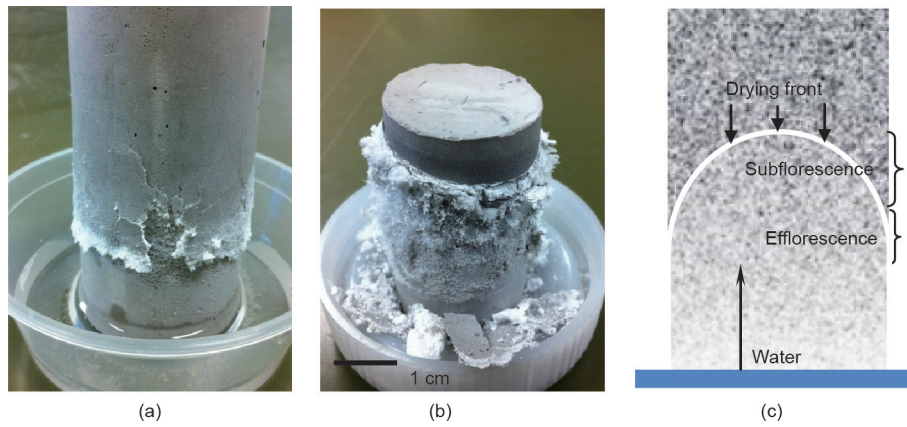


图9. (a) FA基AAM的底部与水接触7 d后的劣化;(b) 底部暴露于模拟风化条件并定期加水90 d后, 低温养护FA基AAM的劣化;(c) 与水接触的FA基AAM的干燥和结晶过程示意。经Elsevier Ltd. 许可, 转载自参考文献[119], ©2018。

表3 影响OPC混凝土抗Cl<sup>-</sup>渗透性能的因素

Factors	Results	Refs.	
Internal factors	Adsorption of cementitious materials	OPC itself has a certain adsorption effect on Cl <sup>-</sup>	[131]
	Water-cement ratio	The Cl <sup>-</sup> diffusion coefficient increases with an increase of the water-cement ratio	[132,133,134]
	C <sub>3</sub> A content	There is higher resistance of chloride attack with an increase of C <sub>3</sub> A content	[129]
	Pore characteristics	There is worse resistance to chloride penetration with higher pore connectivity and larger pore size	[135]
External factors	Mineral admixture	Mineral admixtures can refine the pore structure of concrete and reduce the chloride penetration rate	[130,133]
	Corrosion time	The apparent diffusion coefficient decreases with the increase of corrosion time	[131,133,134]
	Ambient temperature	The Cl <sup>-</sup> permeability rate increases with the increase of temperature	[131,136,137]
	Stress	In the state of compressive stress, the diffusion coefficient is smaller than in the unstressed state; in the tensile stress state, the diffusion coefficient is larger than in the unstressed state	[131]
	Cracking	There is an increased Cl <sup>-</sup> diffusion coefficient of concrete in the crack area	[131]

程, 是扩散、毛细吸附、渗透等传输形式的综合行为[131]。影响OPC混凝土抗Cl<sup>-</sup>渗透性能的因素[129–137]如表3所示。

AAM的孔隙结构致密, 孔隙溶液的化学组成较为复杂, Cl<sup>-</sup>渗透性与孔隙之间的关系遵循OPC系统相似的规律[138]。AAM具有优异的抗Cl<sup>-</sup>渗透性能。例如, 在相同强度等级下, FA基AAM混凝土的Cl<sup>-</sup>渗透系数是OPC混凝土的1/3 [139]。目前水泥基材料的Cl<sup>-</sup>传输试验方法主要是自然扩散法和加速扩散法[132]。这些方法是否可以被直接用于检测AAM的抗Cl<sup>-</sup>渗透性能还有待进一步检验。

研究人员[140–148]系统研究了AAM抗Cl<sup>-</sup>渗透性能的影响因素(表4和图10)。Zhou [149]发现, 随着NaOH溶液浓度的增加, FA基AAM中溶解的Si和Al越多, 而且在AAM基体中进行的缩聚反应更加彻底, 从而有效降低孔隙率和Cl<sup>-</sup>渗透率。高钙AAM的抗Cl<sup>-</sup>渗

透性能一般优于OPC。随着龄期的增长, 与OPC相比, AAS的耐久性能优势更加明显[150]。Shi等[151]指出, 在Cl<sup>-</sup>渗透的早期阶段, AAS的产物C-(A)-S-H凝胶和水滑石相能吸附Cl<sup>-</sup>, 而且游离Cl<sup>-</sup>较少, 因此早期的钢筋并没有明显的锈蚀现象。

Chen等[152]发现, 在AAS中Cl<sup>-</sup>的渗透主要依赖于连通孔, 而硅灰作为矿物掺合料被掺入AAS, 可以在体系中高度分散, 从而有效填充孔隙, 并在增加致密性的同时有效细化孔径, 进而明显改善抗Cl<sup>-</sup>渗透性能。Zhang等[153]将锂矿渣掺入AAS中明显提高了其抗Cl<sup>-</sup>渗透性能, 原因在于锂矿渣能够增强结构对Cl<sup>-</sup>的吸附作用, 并且磨细的锂矿渣能够填充混凝土孔隙, 使混凝土结构更加致密化。此外, Khan等[154]通过研究发现, 由于AAS产物中含有类水滑石相, 与OPC相比, AAS具有更好的Cl<sup>-</sup>吸附能力。同时, 他们报道了在碱激发矿渣体系中存在两种次要的层状双氢氧化物(LDH)产

表4 影响AAM抗Cl<sup>-</sup>渗透性能的因素

Influencing factor	Results	Refs.
Type of activators	The penetration of chloride in AAM activated by sodium silicate powder is much higher than that of water glass The penetration of chloride in KOH- and NaOH-activated AAM is similar to that in OPC. When CH is used as an activator, the corrosion resistance is improved (Fig. 10)	[140] [141]
Type of raw materials	AAS has better anti-chloride penetration than FA-based AAM under the same conditions	[142]
Content of raw materials	The chloride penetration of AAMs decreases with the increase of raw materials	[140]
Content of alkali	Very complex; no obvious trend	[140,143,144]
Modulus of water glass	An appropriate modulus of water glass can increase the density of AAMs, which is beneficial to reduce the penetration of chloride	[145] [146]
Content of water	Low water content of the matrix will help improve anti-chloride penetration; this trend is in agreement with OPC systems	[147,148]

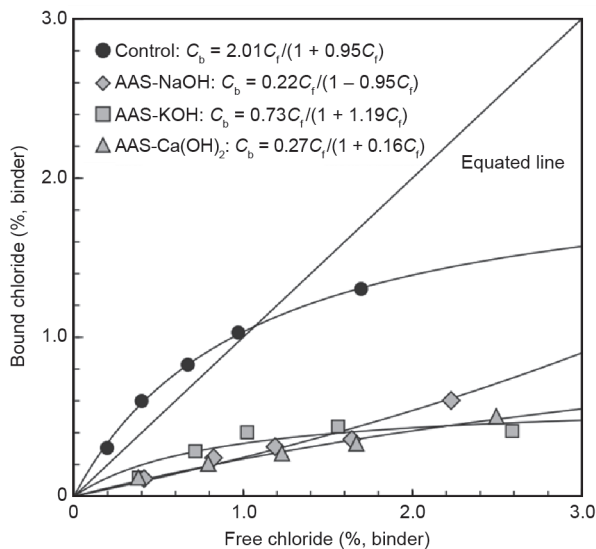


图10. 基于AAS激发剂种类的自由氯化物和结合氯化物之间的Langmuir等温线[141]。C<sub>b</sub>: 结合氯化物浓度; C<sub>f</sub>: 自由氯化物浓度。

物, 即镁铝水滑石和钙铝黄长石, 两者均有固定Cl<sup>-</sup>离子的能力, 但固定机理不同, 前者主要取决于水滑石的表面吸附作用, 而后者在于与Cl<sup>-</sup>反应形成了含氯水铝钙石及其离子交换能力[155]。

## 6. 结论与展望

本文对比介绍了AAM材料和OPC体系在硫酸盐侵蚀、酸侵蚀、碳化和氯化物渗透方面的耐久性能研究的最新成果。根据文献和讨论可以得出以下结论:

(1) 通常, AAM比OPC表现出更好的耐久性能。然而, 由于反应产物的不同, 无钙或低钙AAM和高钙AAM在特定耐久性能研究方面显示出显著差异。无钙AAM的主要产物N-A-S-H凝胶在化学侵蚀作用下引发

的强度损失、孔隙结构变化和化学侵蚀导致结构缩聚开裂等, 其劣化机理与高钙AAM的主要产物C-(A)-S-H凝胶不同。此外, 由于高钙AAM(如AAS)的主要产物类似于水泥水化产物, 所以二者及其制备的混凝土在碳化、酸侵蚀与硫酸盐侵蚀过程中的劣化机理也存在一定的相似性。

(2) 越来越多的固体废弃物被作为硅铝质原料来制备AAM, 这些原料不再仅仅是MK、FA和SG。目前, 利用固体废弃物的核心目标是循环利用。到目前为止, 制定指导固体废弃物利用相关标准的精力还不足。原料中其他组分(如MgO)会对AAM的性能造成未知的影响, 这值得业界关注并在今后进行深入研究。

(3) 目前整个建筑行业针对AAM耐久性能的研究测试方法仍普遍采用OPC水泥和混凝土的检测方法。然而, 二者在反应机理、生成产物和微观结构方面都不相同, 能否直接采用尚有争议, 需要在实验室和实际工程研究中进一步验证(只有使用足够体积的AAM进行实验才更加客观)。

(4) 一些耐久性能提升技术可以改善AAM的性能, 主要包括提高反应聚合度、改善孔隙结构和提高结构密度等。通过在AAM中加入适量纳米SiO<sub>2</sub>可改善产物微结构和提高其抗碳化性能。LDH具有层间离子交换能力, 可以吸附通过孔隙渗透到胶凝材料内部的Cl<sup>-</sup>和其他侵蚀离子。将LDH掺入AAM中对改善其耐久性能具有很大的潜力。

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## Compliance with ethics guidelines

Aiguo Wang, Yi Zheng, Zuhua Zhang, Kaiwei Liu, Yan Li, Liang Shi, and Daosheng Sun declare that they have no conflict of interest or financial conflicts to disclose.

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