TURBULENCE MEDIATED RAPID ALUMUINOSILICATE FORMATION IN HYDROTHERMAL VEIN BRECCIA: NGATAMARIKI GEOTHERMAL POWERSTATION, NEW ZEALAND

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ABSTRACT

A recent cleanout of a geothermal brine-pentane heat exchanger at the Ngatamariki geothermal power station provides valuable insight into the in-situ formation processes of both hydrothermal vein breccias and geothermal aluminosilicate scales. Samples of the scale breccia taken during the cleanout primarily consist of broken fragments of a dark-coloured amorphous aluminosilicate pipe scale, which was remobilised and redeposited within the heat exchanger over a period of ~12-hours during the early stages of the breccia forming event. This dark coloured clastic component was subsequently cemented with a white-coloured, massive to very fine-grained amorphous aluminosilicate matrix over the course of weeks. Scanning Electron Microscope (SEM) analyses indicate that the dark component of the breccia formed relatively slowly via colloid impact as a pipe-wall scale before separating from the pipe wall prior to its remobilisation. In contrast, the white fraction of the breccia appears to have precipitated quasi-instantaneously in place, likely as a result of the turbulence induced flashing caused by the earlier deposited clastic scale obstructing flow into the heat exchanger tubes. The rapidly formed white aluminosilicate fraction served to seal voids within the breccia, forming a strong cementing matrix. The volume and rate of white amorphous aluminosilicate precipitation was significant, with the breccia consisting of up to ~20vol.% white aluminosilicate matrix. A fine white aluminosilicate powder discovered immediately downstream of the breccia appears identical to the white aluminosilicate breccia cement, although unlike the aluminosilicate cement it contains ≥4 w.t.% of the aluminium oxyhydroxide mineral, boehmite. Knowledge gained from the investigation of this event yields invaluable information, both for the prevention of similar scaling events in the future, and the understanding the formation mechanisms of geothermal aluminosilicate scales generally. Furthermore, this event provides unique insight into the interaction between some physical and chemical processes which also occur within active natural hydrothermal systems.

1. INTRODUCTION

Breccias are ubiquitous features of veins within both active and extinct hydrothermal systems, (Jébrak, 1997), and are frequently the target of epithermal mineral exploration (Jébrak, 1997; Corbett, 2002). Brecciation events occur during both the initial formation of veins via tectonic, hydraulic, or phreatic forces, and during their subsequent evolution via processes such as mineral deposition, collapse, chemical and physical erosion, and dilation via continuing tectonic and hydraulic forces (Jébrak, 1997). Direct observation of these processes within active hydrothermal systems poses obvious technical challenges though, with most of the knowledge regarding them obtained from the study of ancient deposits from extinct epithermal systems. Geothermal pipelines and vessels can, however, provide useful and accessible, simplified artificial analogues of a natural hydrothermal vein systems. These pipelines and equipment replicate many important processes which occur within natural hydrothermal systems such as rapid boiling, gas exsolution, rapid cooling, mixing of fluids of different temperature and chemistry, as well as hosting a wide variety of fluid flow regimes. These attributes have the potential to offer unique insights into processes which would otherwise occur in locations well beyond normal reach.

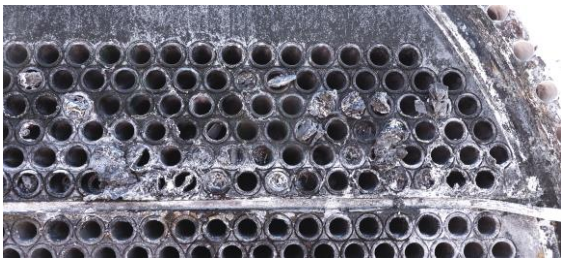

Fig. 1. Blocked first pass tubes of the OEC1 superheater vessel, Ngatamariki Geothermal Power Station.

An event following a shut of Ormat Energy Converter 1 (OEC1) at Ngatamariki Geothermal, New Zealand, provides such an insight. This OEC unit, one of four OECs at Ngatamariki, was shut down for several days in mid-January 2020 to facilitate the replacement of its pentane turbine bearings, with three of its four brine heat exchangers also opened for inspection and cleaning while the unit was offline. Although two of the three vessels were relatively clean, a significant number of the first-pass tubes of OEC1's superheater (Fig. 1) were observed to be blocked with scale prior to cleaning. The superheater vessel of each OEC is the first heat exchanger through which separated hot brine passes at Ngatamariki, and similar observations of superheater first-pass scales had been made during previous shut cleans. These scales are formed from broken dark-coloured clasts and flakes, which originally formed upstream of the superheater, prior to being remobilised, lodged, and cemented within the tubes by a white-coloured material (Fig. 2). Samples of these tube obstructing scale clasts and in-situ deposited wall scales were taken before the unit was cleaned via hydro-blasting, prior to being put back into service.

Three days after OEC1 was restarted on January 20th, a transient disruption and resumption in brine flow was followed by a rapid increasing trend in differential pressure (dP) measured between the brine inlet and brine outlet of the OEC1 superheater. The initial dP rapid elevation phase continued for 12 hours, with brine dP across the superheater increasing from approximately 1.4 to 2.6 bar during this period (Fig. 3).



Fig. 2. Dark coloured scale fragments cemented with white material in the OEC1 superheater first-pass tubes, observed in mid-January 2020. Both the dark coloured and light-coloured scales are hard and mechanically strong.

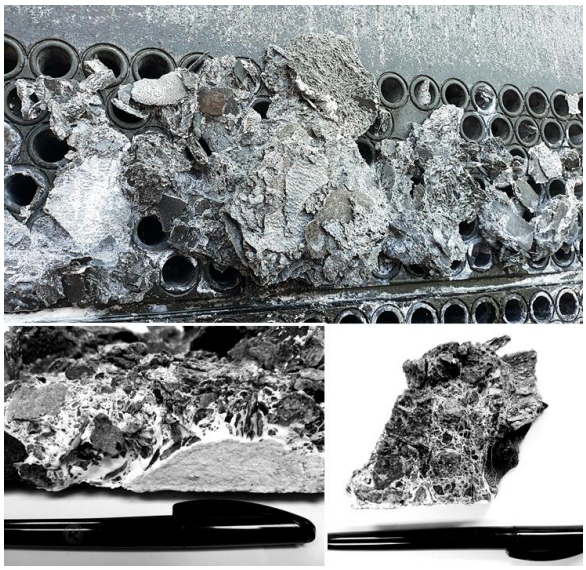

Fig. 4. Some of the material found blocking the OEC1 superheater first-pass tubes in April 2020. Top image: Scale in place, cemented to tube sheet. Bottom images: Hand specimens taken from the first-pass tube sheet/inlet section of superheater endcap. The white cementing material is somewhat powdery on the scale's bottom edge (near the pen used for scale) but is hard and smooth on most of its exposed surfaces.

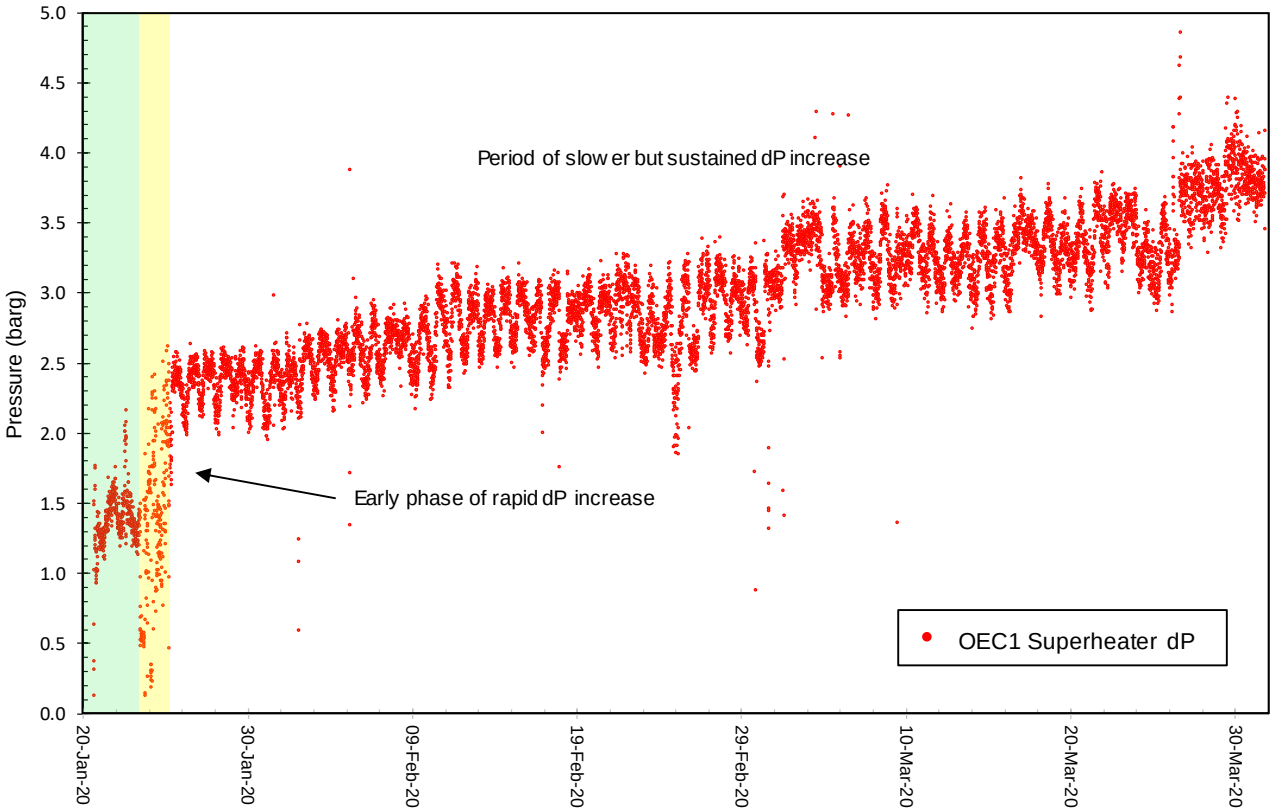

Fig. 3. Brine differential pressure between the inlet and outlet of the OEC1 superheater vessel between being restarted on the 20th of January and the 31st of March. The green bar indicates the period of normal superheater operation following the restart of OEC1 and prior to the rapid dP increase event, with the yellow bar indicating the onset and initial phase of the superheater dP increase event.

This 12-hour long phase was followed by an abrupt step-change to a much slower rate of dP increase which continued for approximately 10 weeks, with dP increasing from ~2.6 to ~4 bar during this time (Fig. 3). This increase in brine superheater differential pressure was maintained until the unit was shut down for cleaning another 2 weeks later. Based on previous observations of the heterogeneous nature of Ngatamariki superheater scales, it was suspected that the two distinct dP trends separated by the sudden step change may represent two separate scaling mechanisms. In more detail, the working hypothesis prior to opening the vessel was that the initial rapid 12-hour dP increase may have been due to the accumulation of remobilised scale clasts and fragments within the superheater, with the subsequent slower trend representing the infilling and cementation of this clastic material via some in-situ precipitation reaction. The second part of this hypothesis was much less certain given the relatively short time period of the event, and the significant rate of deposition necessary to have such a significant effect on superheater dP, however.

Once shut down, the superheater vessel was again carefully inspected, with scale samples gathered prior to cleaning. Upon opening, a significant quantity of pre-formed dark-coloured scale fragments and cemented lumps were observed to be blocking the first pass of the superheater tube sheet (Fig. 4), with a significant amount of this material also lodged within the first-pass tubes. Of even greater interest was the presence of a significant volume of white-coloured cementing material, which appears to have been rapidly precipitated in place, or in very close proximity to the surface of the dark-coloured clastic scales (Fig. 4). This white material was also found deposited downstream of the first-pass tubes within the remainder of the superheater as a fine white powder, with the greatest abundance observed mantling the horizontal divider plate immediately downstream of the first-pass tubes (Fig. 5). No sign of this white powder was observed upstream of the first-pass obstructing scales, however, indicating the nucleation point of this material was the tube-face scale breccia itself.

The conditions under which this rapid scaling event occurred are well constrained in terms of both the physical and chemical conditions under which it took place, and the time over which it transpired. This event, therefore, offers a unique opportunity to both develop measures to more successfully mitigate similar scaling occurrences in the future, and to gain insight on similar physicochemical processes which are likely ubiquitous deep within natural hydrothermal systems.

2. METHODS

Three scale samples were taken from the OEC1 superheater during the January 2020 shut, and further nine during the April shut (Table 1.). All samples were analysed via X-ray fluorescence (XRF) and ten via X-ray diffractometry (XRD) at the University of Waikato, with one examined via Scanning Electron Microscopy (SEM) using Energy-Dispersive X-ray Spectroscopy (EDS) at the University of Auckland. The aim of the XRF and XRD analyses was largely to determine whether rock fragments washed up from the production reservoir were a significant contributor to the scales, or if the material was instead amorphous, and likely precipitated from the production fluid itself. The purpose of the SEM analyses was to determine the microstructure of the scale, any chemical zonation, and textures which may indicate deposition mechanisms. The fragment of dark-coloured scale selected for SEM analysis was fractured perpendicular to the fluid-facing surface and mounted with this fractured face pointing upwards so that the full cross-section of the scale fragment could be analysed, including areas of both its topmost and basal surfaces.



Fig. 5. White powder found downstream of the first-pass tube blockage. Top image: Middle divider plate. Bottom left image: Western endcap drain. Bottom right image: Middle divider plate edge close-up view.

3. RESULTS

The particle size of the dark-coloured scale fragments, which make up the bulk of the scale breccia, ranges from sand size, up to ~50mm, while the white-coloured cementing material is very fine grained, hard and massive, though is slightly powdery at its surface. Tube blocking scales and many of the cemented scale masses observed during the January shut, as well as during previous shut inspections of this and other Ngatamariki OECs, also share these features, though they generally occur at a smaller scale. Particularly, the white clast-cementing material found during the April 2020 shut also features in superheater tube blocking scales observed during previous shut inspections (Lawson, 2014; Richardson, 2014; Clark, 2017).

All scales sampled during the January shut inspection consist of amorphous aluminosilicate (Table 2 and Fig. 7) with minor calcite (washed in from the production wells), iron sulphides, and quartz [likely a product of the recrystallisation of the amorphous silica fraction of the scale, (Simmons et al., 2000)]. Similarly, the samples collected during the April shut also largely consist of amorphous aluminosilicate, along with the same accessory phases, that is with the noteworthy exception of sample EDV1. This material is the fine white powder which was found mantling the middle divider plate (Fig. 5) immediately downstream of the first-pass tubes (Fig. 6), and hence the first-pass tube blocking scales. This powder has a similar chemical composition to the other aluminosilicate scales sampled from the superheater during the April shut, although with a greater concentration of Al (Table 2) at 13.2 wt.% Al_2O_3. Structurally, this material appears to be similar to the other aluminosilicate scales from the January and April scale sample sets, being dominantly amorphous, and possessing a very similarly shaped X-ray diffraction pattern (Fig. 7 and 8). The significant difference between this material and the other largely amorphous aluminosilicate scales is the presence of the aluminium oxyhydroxide phase, boehmite (Fig. 8).

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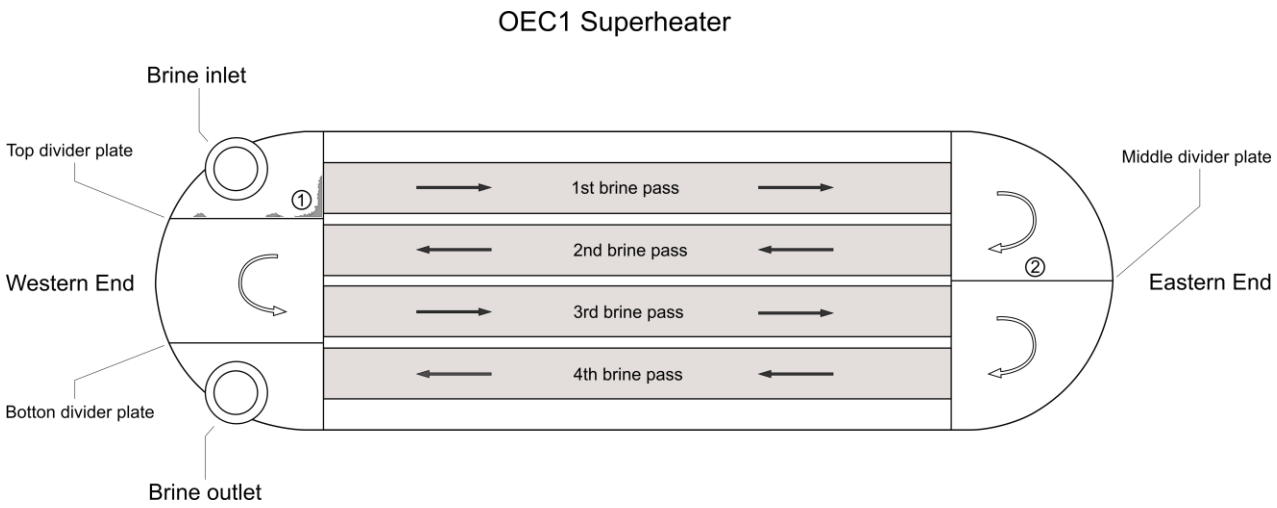

Fig. 6. Schematic illustration of the Ngatamariki OEC1 superheater. The unit is a four-pass design with the brine entering at the top of the western endcap and exiting at the bottom of the same end. 1: Location of tube-blocking scale masses in inlet/first-pass section of the heat exchanger. 2: Middle divider plate in eastern endcap where the largest quantity of white powder material was found (sample EDV1).

Table 1. Descriptions and analysis techniques for January and April 2020 OEC1 superheater scale samples.

Code	General location	Specific location	Scale description	Methods
SH1	West (inlet-outlet) end	Inlet section of end cap	Dark grey fragments cemented with white material	XRF, XRD, SEM
SH2	"	Third pass tube face	Light grey fragments cemented with colourless material	XRF
SH3	"	Outlet section of end cap	Light grey fragments cemented with colourless material	XRF

April 2020 samples

Code	General location	Specific location	Scale description	
WFP1	West (inlet-outlet) end	Inlet/first pass tube sheet	Dark grey fragments cemented with white material	XRF, XRD
WFP2	"	Inlet/first pass tube sheet	Dark grey fragments cemented with colourless material	XRF, XRD
WFP3	"	Inlet section of end cap	Dark grey fragments cemented with colourless material	XRF, XRD
WFP4	"	Inlet section of end cap	Very hard mass of cemented fragments with black coatin	XRF, XRD
ESP1	"	Second pass tube sheet	Dark grey flakes, vitrous top surface,	XRF, XRD
EDV1	East (turnaround) end	Divider plate	Fine white power which disolves in acid	XRF, XRD
BC1	Blaster cuttings	Hydro-blasting debris trap	Translucent grey sand size particles	XRF, XRD
BC2	"	"	Translucent grey sand size particles	XRF, XRD
BC3	"	"	Translucent grey sand size particles	XRF, XRD

Table 2. Elemental compositions (oxide wt.%) of OEC1 superheater scale samples as determined via XRF.

January 2020 samples

Sample	SiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)	CaO (%)	Fe_2O3 (%)	MgO (%)	MnO (%)	S	Cu
SH1	69.67	15.93	3.51	4.61	3.64	2.51	0.11	0.03	3820	1350
SH2	82.38	9.82	2.42	2.93	2.02	0.40	0.00	0.03	570	2800
SH3	84.59	8.45	2.11	2.53	2.01	0.28	0.00	0.03	410	220

April 2020 samples

Sample	SiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)	CaO (%)	Fe_2O3 (%)	MgO (%)	MnO (%)	S	Cu
WFP1	68.47	10.14	2.14	2.56	3.85	2.70	0.26	0.05	9242	2538
WFP2	69.38	9.56	2.07	2.46	3.94	2.49	0.21	0.05	8859	1764
WFP3	69.27	9.25	2.17	2.29	3.11	4.14	0.41	0.07	15469	4373
WFP4	63.67	10.18	2.03	2.28	6.61	3.68	0.44	0.07	11224	1537
ESP1	69.48	9.73	2.08	2.50	3.53	2.50	0.28	0.05	8923	2452
EDV1	66.65	13.21	1.97	2.80	2.01	1.67	0.08	0.02	7146	1948
BC1	70.84	11.39	2.40	3.02	2.17	0.96	0.06	0.02	4260	1958
BC2	71.37	11.37	2.40	3.00	2.20	0.92	0.07	0.02	4408	1556
BC3	70.78	11.42	2.38	3.00	2.18	1.09	0.08	0.02	3605	1713

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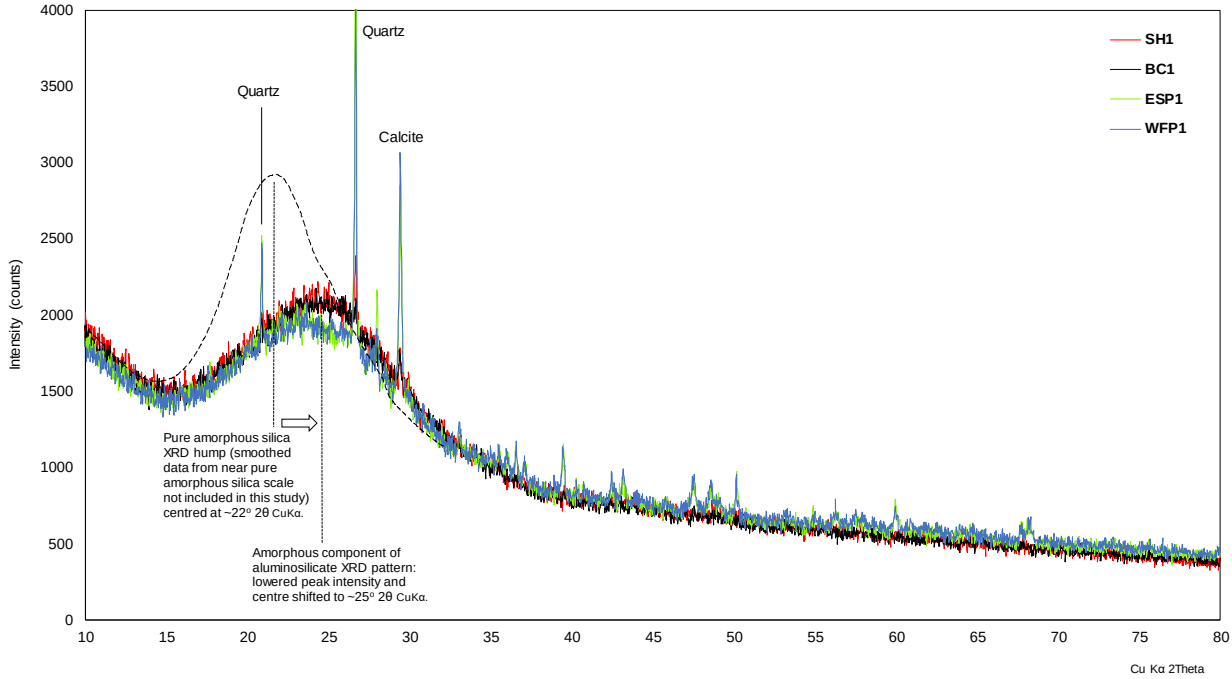

Fig. 7. A selection of XRD patterns from OEC1 superheater scales. The scales are dominantly amorphous aluminosilicate with minor calcite and quartz. Quartz peaks are as a result of recrystallisation of the silica component of the scale, with samples ESP1 and WFP1 appearing to have recrystallized to a greater extent than samples SH1 and BC1. The amorphous component of the aluminosilicate XRD patterns is broader, of lower intensity, and centred at greater 2θ angle compared to that of near-pure amorphous silica (black dashed line), analysed as a part of the same batch as the aluminosilicate scales.

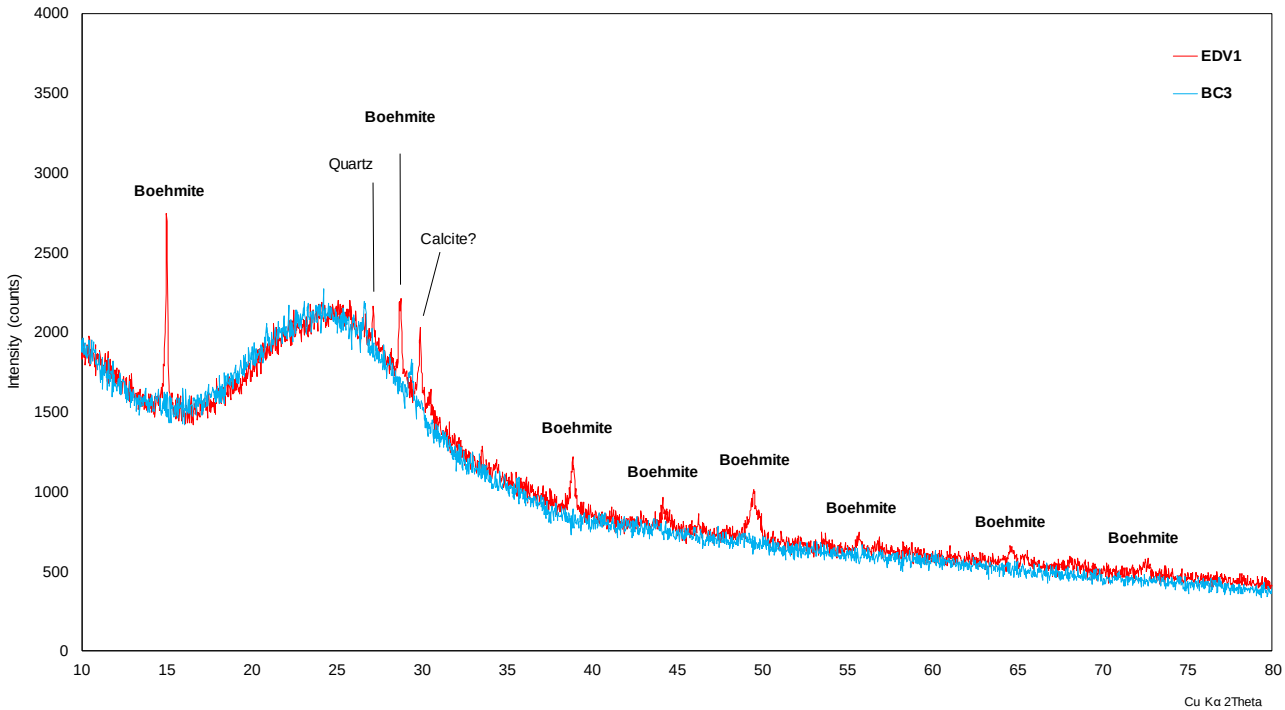

Fig. 8. Sample EDV1 and BC3 XRD pattern comparison. Sample BC3 consists of tube obstructing scale removed via hydro-blasting during the April 2020 superheater clean and is representative of other amorphous aluminosilicate scales sampled from the OEC1 superheater during both 2020 shut inspections in terms of its composition and likely short-range structure. The chemical composition and XRD patterns of both the EDV1 and BC3 samples are also near identical, except for the distinct boehmite peaks of the EDV1 diffraction pattern. Some very subtle diffraction intensity features within the BC3 XRD pattern indicate that this sample may also host minor quantities of boehmite, however this could be due to small quantities of the fine white EDV1 type powder also caught in the hydro-blaster cuttings trap. The particles caught in the trap were mostly sand-sized, with almost no material any finer than this retained by the mesh used to intercept sample material, however.

Table 3. Results of mole charge balance calculations based on the assumption that metal cations (Na+, K+, and Ca2+) balance a -1 charge per mole of tetrahedrally coordinated Al substituting for Si in a tetrahedral silicate structure.

Sample	(Na+K+2Ca)/Al	Comment	Calcite %
SH1	1.09	Excess Ca: Calcite	1.4
SH2	1.10	Excess Ca: Calcite	1.0
SH3	1.17	Excess Ca: Calcite	1.4
WFP1	1.31	Excess Ca: Calcite	3.1
WFP2	1.38	Excess Ca: Calcite	3.6
WFP3	1.27	Excess Ca: Calcite	2.4
WFP4	1.75	Excess Ca: Calcite	7.5
ESP1	1.29	Excess Ca: Calcite	2.8
EDV1	0.75	Excess Al: Boehmite	nd
BC1	0.98	Balanced: No calcite	nd
BC2	0.99	Balanced: No calcite	nd
BC3	0.97	Balanced: No calcite	nd

This phase appears to be relatively abundant within the material, with ≥25% of the Al within the EDV1scale likely in the form of boehmite, based on mole charge balance calculations (Table 3), yielding a boehmite concentration of ~4 w.t.%. The EDV1 sample also appears to contain calcite, so this estimate is likely an underestimate. Following these surprising results, subsamples of the white aluminosilicate cementing material from two large pieces of tube blocking scale collected during the April shut were separated and analysed via XRD to determine whether this material also contained boehmite. Although the XRD patterns produced by these samples were identical to the EDV1 sample in all other respects, no obvious sign of boehmite structure was evident in this hard, cementing material.

As for the dark component of the breccia, surface micro-textures textures of the scale observed via SEM analysis (Fig. 9) indicate that, despite the scale's vitreous appearance, this material was deposited via colloid impact and agglomeration from aluminosilicate sols transported in the geothermal brine. Although not detectable via XRD, rare fragments of formation material containing minerals such as illite were also observed, as were iron oxides, and a relative abundance of sulphide minerals; the latter of which likely impart the dark grey colouration of this scale. Along with the relatively uniform curvature and 2 to 5mm thickness of the individual plates which make up the dark-coloured scale, the results of the SEM analysis indicate that this material likely formed relatively slowly via colloid aggregation as a pipe-wall scale, upstream of the superheater in the hot-brine pipeline.

4. DISCUSSION

Given the significant and rapid increase in brine dP across the superheater during the first 12 hours of the January 23rd event (Fig. 3), it is likely that a large proportion of the scale breccia observed when the vessel was opened in April was deposited during this initial phase. It is suggested that the transient disruption and resumption of brine flow immediately prior to this event may have remobilised loose material in the hot brine line upstream of the OEC1 superheater. This line had also been shut down for the January OEC1 shut work, so pipe wall scales may have been loosened due to thermal contraction of the line during this time. From brine pressure data captured by the plant's distributed control system (DCS) (Fig. 3), this initial phase of rapid clastic scale accumulation appears to have

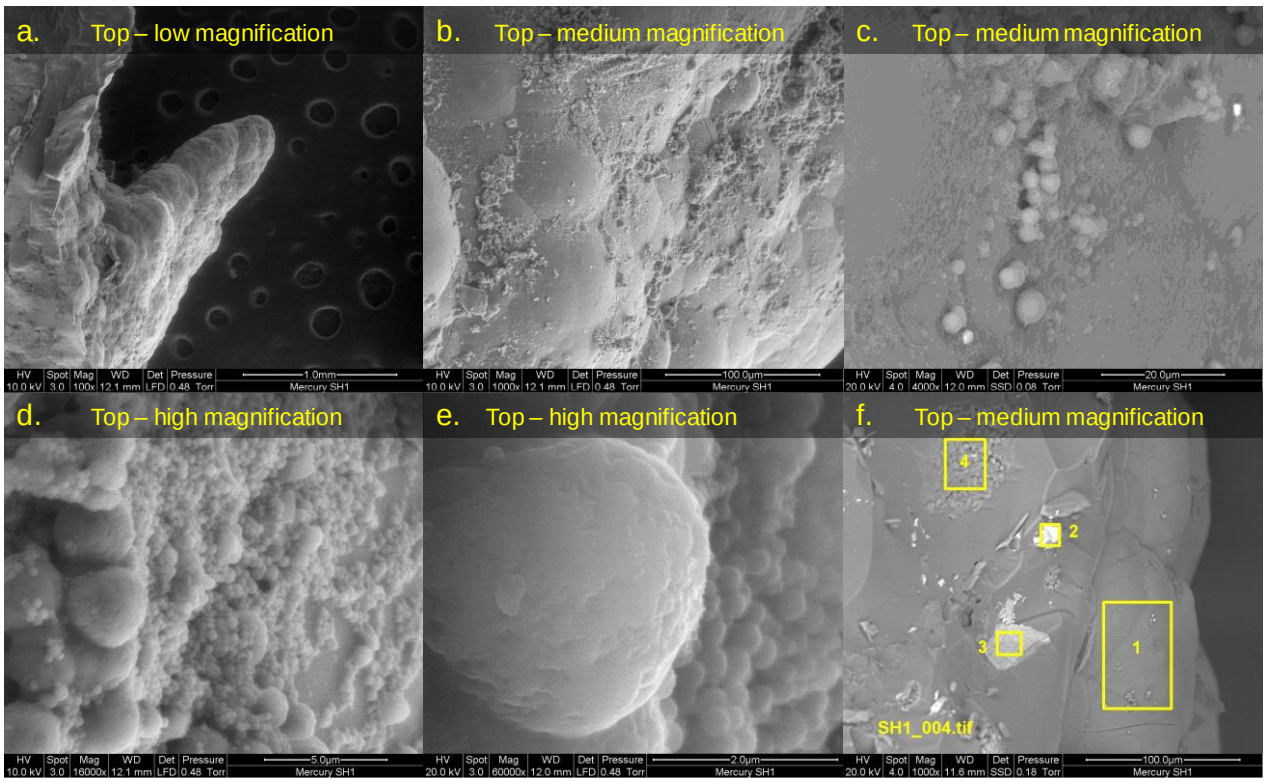

Fig. 9. SEM images of the dark coloured siliceous component of sample SH1. a: top surface of the SH1 scale fragment (top to right in all images). b, c, d, e: small colloids visible on the top surface of the SH1 scale sample. f: fragments of other materials suspended within the aluminosilicate scale; 1: aluminosilicate scale free of other materials, 2: iron sulphide mineral, 3: iron oxide, 4: potassium rich clay, likely illite.

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concluded relatively abruptly after approximately 12 hours. This phase of the event may be somewhat analogous to the migration of clastic material created by tectonic or hydraulic dilation/reactivation of a hydrothermal vein.

The next phase of the event was characterised by a slower but almost continuous increase in brine dP across the superheater vessel (Fig. 3). It is suggested that it was during this phase of the event that the white aluminosilicate cement and fine white powder were being formed. Based on our observations, these materials are most likely equivalent, with the white powder being the original substance from which the white cementing material was formed in a continuous process. Following its rapid precipitation, much of the white powder likely remained suspended within the brine, travelling through the superheater and beyond, with only a small proportion intercepted by the breccia to form the white cement. The retained cementing material then had the opportunity to continue its structural and chemical evolution in-place toward a more thermodynamically stable form (boehmite is not stable in aqueous silica-rich environments) over the following days and weeks. In contrast, the sample EDV1 powder was likely very recently formed, as it seems unlikely that this loose fine powder would have a residence time of any significant duration on the relatively smooth surface of the superheater divider plate, given the velocity and turbulence of the brine as it changes direction between the 1st and 2nd superheater passes. The EDV1 powder is therefore much more likely to retain its juvenile character, compared to the older (but equivalent) aluminosilicate breccia cement. Thus, this material still contains boehmite, which had yet to be completely consumed by silica. A similar phenomenon was observed by Yokoyama et al. (1999) in aluminium-containing silica scales from Hachobaru geothermal power station in Kyushu, Japan. Within this material, the recently deposited scale was found to contain a significant portion of octahedrally coordinated Al, which was rapidly converted to tetrahedral coordination deeper within the same deposit. The EDV1 aluminosilicate powder also bears a close similarity in terms of composition and likely short-range structure to rapidly precipitated synthetic geothermal aluminosilicate produced in recent lab experiments (Newton, 2020) (Table 4). The chemical trigger for the quasi-instantaneous precipitation of this synthetic aluminosilicate material was found to be the supersaturation of aqueous Al with respect to boehmite; with this reaction proceeding independently of silica concentration in the test brines (Newton, 2020). Given the presence of the significant boehmite fraction in the EDV1 aluminosilicate, the extreme rapidity of its precipitation, and the silica-undersaturated conditions (SSI ~0.87) of the OEC1 hot brine line/superheater inlet, it seems highly plausible that this same chemical mechanism also resulted in the formation of the EDV1 powder, and therefore the white breccia cementing aluminosilicate.

In contrast to the chemical mechanism, the precise physical mechanism which triggered the production of this material is less certain, although it is suggested that it may be micro-flashing induced by the turbulence and rapid pressure drop clastic scale at the first-pass tube face. Localised rapid, transient, brine cooling and concentration resulting from this turbulent flashing may have caused the precipitation of boehmite nano-sols, and hence the formation of amorphous geothermal aluminosilicate (Newton, 2020). Boehmite is saturated to slightly supersaturated at the inlet of the OEC1 superheater, so flashing or other disturbance could quite conceivably result in its precipitation. Given the exceptionally strong signal of the presence of boehmite in the EDV1 XRD data, this appears to have indeed occurred here.

Table 4. Compositional comparison between EDV1 powder from OEC1 and rapidly precipitated synthetic aluminosilicate (AS) produced in lab experiments (80F02, Newton, 2020). Ratios calculated on a mole basis.

Material	Si/Al	(Na+K+2Ca)/Al	$(K/Na_{(scale)})/(K/Na_{(brine)})$
EDV1 powder	4.3	0.75	7.45
Synthetic AS	3.6	0.78	7.29

5. CONCLUSION

These observations provide important insights into the interaction between physical and chemical processes within both active natural hydrothermal systems, and man-made geothermal energy infrastructure. This series of physical and chemical scaling events within the OEC1 superheater was triggered solely by a physical mechanism – the remobilisation of clastic material within the hot brine line due to a transitory brine flow disturbance. The resulting rapidly accumulated breccia at the superheater tube-face subsequently triggered a chemical reaction which cemented the clastic scale and caused the rapid infilling of the remaining void-spaces within the breccia. This reaction likely positively fed back into itself as the solid material produced by the reaction further added to the flow-obstructing breccia, and the resulting pressure drop across it. The final result of these processes was a cemented breccia that bears a striking resemblance to many vein breccias found in fossil hydrothermal deposits.

Similar processes may also be responsible for other instances of aluminosilicate scaling in geothermal pipelines, particularly instances where it occurs early in the brine/two-phase fluid flow path, such as at or near geothermal production well heads (Newton 2020; Newton et al., 2018; Raymond et al., 2005, Reyes et al., 2001). Several instances of these scales appear to be formed from aluminosilicate sols bought up production wells from the reservoir (Newton 2020; Raymond et al., 2005), with at least one of these displaying evidence of aluminosilicate scaling within the production reservoir itself (Raymond et al., 2005). Once again, the turbulent flashing of deep hydrothermal fluids (this time within the within the production formation) may be resulting in the transient supersaturation of Al with respect to boehmite, and therefore the quasi-instantaneous seeding of aluminosilicate sols and the subsequent scaling of geothermal infrastructure further down the fluid flow-path.

Rapid colloidal aluminosilicate deposition events may also occur within natural hydrothermal breccias formed via hydraulic or tectonic forces within boiling, high fluid-flow environments (Marinova et al. 2014). Simultaneously, such events, resulting in the precipitation of boehmite sols, may also result in the rapid deposition of colloform aluminosilicate material on down-steam vein walls with material equivalent to the EDV1 powder. Namely, this process could be a mechanism for the deposition of aluminosilicate mineral rich bands in deposits such as colloform and crustiform quartz-adularia veins (Marinova et al. 2014: Simmons et al., 2000), which have been previously recognised as being the recrystallised ancient equivalent of amorphous geothermal silicate scales (Marinova et al. 2014; Simmons et al., 2000).

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6. FUTURE WORK

The fascinating observations offered by this event deserve further investigation, both to help prevent future similar scaling events, and in a bid to further enhance understanding of aluminosilicate scaling processes more generally. Further research of this phenomenon also has the potential to reach beyond the geothermal energy industry and reveal details of deep subsurface processes occurring within ore-forming natural hydrothermal environments. In particular, the sample EDV1 aluminosilicate powder appears to be new to geoscience, and therefore a more detailed and in-depth characterisation of the white aluminosilicate powder and aluminosilicate cement is required to further understand their chemistry and structure, as well as their evolution with time.

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