

HARD GRAY SCALE

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Abstract

The dry scrubbing and secondary alumina handling systems for pre-bake cell technologies are hampered by accumulations of hard gray scale, or HGS. HGS is an amorphous reaction product formed from collision-induced reactions of bath fines, alumina and water. HGS formation is greatest in high attrition areas owing to the high surface energy of new alumina surfaces created by the fracture of alumina particles. If not systematically addressed with cleaning and maintenance procedures HGS can: greatly reduce the removal efficiency of gaseous fluoride in dry scrubbers, reduce the capability to convey alumina in sufficient quantities, reduce filter life and alter the concentration of fluoride on secondary alumina.

By moving to higher line load and/or pot hooding flow rates an acceleration of HGS formation in dry scrubbers and reacted alumina transport lines is likely, especially when existing equipment is utilized without upgrades. This accentuates the need for counter-measures to reduce or control HGS formation rates. This paper defines the chemistry of HGS, proposes a mechanism for HGS formation, discusses the conditions that are necessary to form HGS, identifies the key areas of concern in a smelter, and discusses practical alternatives to reduce rates of HGS formation.

Introduction

In the aluminum smelting process, individual reduction cells are hooded to collect process gases. Individual pot exhaust duct flows are combined and most typically fed into an alumina-based dry scrubbing system to recover evolved fluorides and process dust. The surface chemistry and reaction mechanism between smelting grade alumina and gaseous fluoride has been characterized previously. [1] The output from the dry scrubbers, a.k.a. reacted, or secondary alumina, is a combination of fluoride enriched alumina and bath fines that are returned to the smelting cells during pot-feeding to recycle captured fluoride and dust.

These closed-loop recycling systems are a cost-effective means for minimizing fluoride emissions, since no waste is created by the process. Regulatory requirements and increases in pot line load present ever-increasing demands to improve the efficiency of these systems from both a fluoride capture and a maintenance perspective. A common problem that impacts both scrubber efficiency and maintenance of smelter dry scrubbers is the formation of hard gray scale.

Hard gray scale, HGS, is a term used to describe slate-like scale that forms in alumina-based dry scrubbing systems of all types, and in alumina transport lines and dust collection lines that are downstream of dry scrubbers. The formation of HGS negatively impacts smelting operations by reducing dry scrubber flow and efficiency and by choking off alumina transport system

components. HGS formation can occur in any smelting location, regardless of its base technology (pre-bake or Söderberg) or scrubber technology (fluid bed or injection). However, HGS formation is far more common at pre-bake plants due to the pitch volatile content on the reacted alumina of Söderberg plants. It is also more common to have issues with HGS on injection-based dry scrubbing systems than on fluid bed dry scrubbing systems. The rate of HGS formation also varies from location to location due to differences in environmental and operating factors.

The chemical structure of HGS has been a subject of speculation for years. This material is largely amorphous, thereby precluding phase analysis by X-ray diffraction. Deliberate programs to reduce HGS have been often been limited by a lack of understanding regarding the chemistry or formation mechanism of this material.

The purpose of this paper is to define the chemistry and formation mechanism of HGS. The formation mechanism defined herein was verified by successfully synthesizing HGS from smelting materials in the laboratory. Practical approaches for limiting the rate of HGS formation are proposed.

Discussion

Visual Appearance, Occurrence and Impact of HGS

Samples of HGS were collected from numerous Alcoa smelters, worldwide. These consist of samples collected from the inside of scale-choked pipes and from free-standing pieces found in dry scrubber discharge conveyors and screening devices. Pictures of free-standing pieces of HGS are shown in Figure 1.



Figure 1 – Samples of Hard Gray Scale

These pieces range in color from light to dark gray and are generally slate-like in appearance. The surface contours evidence wear patterns that are aligned with the direction of process gas flow. Accumulations of HGS such as these are also commonly observed on diffuser plates in fluid bed and injection scrubbers, alumina injection points, reacted alumina hopper discharge points

and walls, dirty-side tube sheet thimbles, recirculation orifices, air lift tubes, dust collection ducts and recycle weirs. The accumulation of HGS in orifices that control the flow of recirculated alumina can inhibit or stop the majority of alumina flow in many injection type scrubbers. The net result of HGS scaling is that scrubber efficiency and gas flow may often be significantly reduced.

Figure 2 shows a section of partially choked point feeder transport pipe. The scale buildup had restricted flow to less than 50% of the design rate. Scale buildup will accelerate velocity, amplifying the net attrition of alumina particles, and increasing the rate of HGS deposition. In this case HGS also reduced volumetric alumina flow to point feeders, negatively impacting pot feed control and increasing the incidence of anode effects. The replacement of alumina feed lines due to HGS scaling is a significant recurring maintenance cost at this particular location.

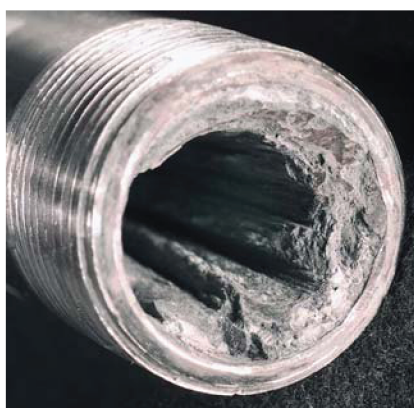


Figure 2 – Photo of a pot feed pipe partially choked with HGS

HGS scaling on fluid bed reactor diffuser plates, or dribble plates, impacts the fluidization dynamics by creating localized “dead zones” where pot room exhaust no longer passes through the alumina bed. The physical impact of HGS on fluid bed scrubber dribble plates is shown in Figure 3.



Figure 3 – HGS plugging dribble plates – 2 months after cleaning

HGS has an equivalent impact on injection scrubbers by choking off the diffuser plates that distribute process gas flow. These components may often be over-looked during routine maintenance of the dry scrubbers and filter bags. Heavy accumulations have been known to reduce system flow rates, increase fluoride emissions from the pot room roof, increase filter chamber pressure drops, cause premature bag failures, blind filter cloth areas and in extreme cases cause the formation of HGS on filter cloth itself. An example of HGS on diffusers is shown in Figure 4.



Figure 4 – HGS on diffuser plates before and after cleaning.

HGS can further impact dry scrubber operations by partially or completely blocking flow control points or orifices for alumina recirculation. The impact of is illustrated Figure 5. Under normal operation, greater than 85% of the total alumina injected into the process gas stream comes from the recycle stream.



Figure 5 – 100% plugged recirculation point (left) and normally functioning alumina injectors (right). Fresh alumina at bottom.

Note that only the alumina injector feeding reacted alumina is affected by HGS scaling, alumina flow has become completely blocked in the example shown above. This observation suggests that there are key components in the reacted alumina stream that are required to facilitate HGS formation.

HGS is commonly observed in high turbulence areas of reacted alumina handling systems where inter-particle contact is most vigorous and where process gas flow rapidly changes direction of flow. Figure 6 shows tube sheet inlet thimbles below shaker bags.



Figure 6 – End-on view of thimble inlets to shaker type bags

This photo was taken from inside the hopper looking straight up at the tube sheet. The bags themselves are above the thimbles and tube sheet and can not be seen in this rather extreme example of HGS blockage that also affected filter bag life.

HGS formation in areas like these is limited to situations where ultra-fine particles and elevated moisture levels are present. The use of moist air, or compressed air with a high dew point, for fluidization of reacted alumina is one example of an operating variable that has been linked with increased HGS formation rates in a bag house.

Chemical Composition of HGS

The chemical composition of hard gray scale collected from several locations is listed below in Table 1. The chemical composition of roof monovent scale and dry scrubber inlet solids are listed for comparison purposes. The crystalline phases observed by XRD in these materials are also listed in Table 1.

Table 1. Elemental and phase composition of HGS, monovent scale and dry scrubber inlet solids.

Element	Fluid Bed 1	Fluid Bed 2	Injection Scr.	Roofline	Dry Scrubber	Synthetic
	HGB	HGB	HGB	Monovent Scale	Inlet Solids	HGB
Al	27	35	25	26	28	33
Na	12	6.4	8.9	5	10	8.1
Si	0.04	<0.02	0.04	0.13	0.04	0.02
Fe	0.35	0.17	0.23	0.27	0.79	0.22
Ca	0.08	0.04	0.61	0.89	1.3	1.2
Mg	<.01	<0.02	0.02	0.09	0.05	0.04
K	1.2	0.35	0.47	0.1	0.31	0.07
Ni	0.29	0.14	0.44	0.08	0.64	0.02
V	0.02	0.02	0.04	<.02	<0.02	<0.02
P	0.06	0.04	0.06	0.05	0.03	<0.02
F	28	16	29.4	30.2	20	20.2
C	1	0.18	3.37	4.2	5.69	
S	0.18			0.02	1.03	0.2
O		26	16.2			
Total Moisture	2.30%			18%		5%
Crystalline Phases	Alpha alumina Minor Chiolite Minor AlF3 Minor NaAlF4	Alpha alumina Chiolite NaAlF4 Minor AlF3	Alpha alumina Minor Chiolite NaAlF4 Minor AlF3	AlF3·3H2O Chiolite Alpha alumina AlF3(OH)x(H2O)y	Alpha Alumina Chiolite Cryolite NaAlF4	Alpha Alumina Chiolite Cryolite

Based on the elemental composition data shown above, alumina (Al₂O₃), sodium, and fluoride account for over 90% of the total mass of hard gray scale generated in dry scrubbers or reacted alumina transport lines. This data suggests that scrubber scale is formed principally from alumina and bath fines together with minor contributions from adsorbed fluoride and bath fume (NaAlF₄). It is interesting to note that the moisture content of dry scrubber scale is roughly equivalent to that expected for fresh alumina. While the phase information presented in Table 1 supports this composition, it is important to note that a significant percentage of HGS consists of amorphous material that does not yield discrete X-ray diffraction patterns.

The composition of particulate solids collected at the inlet to an injection scrubber is shown for comparison in Table 1. This material is chemically similar to dry scrubber scale. The principal difference between these two materials is the higher carbon and sulfur content of the inlet solids. In addition, inlet solids are largely crystalline in nature, since these are particulate solids coming off the pots, giving rise to well-defined and intense X-ray scattering patterns.

Monovent scale is material collected from the point of roof exhaust. Monovent scale is the name given to light gray, hard crusted material often observed coating horizontal surfaces in the roof monovents of smelters. During the filling of open pot feed bins, reacted alumina and bath fines can rise to the pot room roof line. They either exit the smelter as particulate emissions or deposit on horizontal surfaces near the roof line. This material readily absorbs moisture, as evidenced by its high water content

and “cement” in place. The solidification of this material occurs via inter-particle reactions initiated by re-hydration of the surface aluminum fluoride layer of the alumina superfines. It is important to note that monovent scale is not formed in the same manner as dry scrubber scale. Monovent scale results from the hydration-induced solidification of alumina and bath superfines in a low turbulence area (roofline) of the smelter. Monovent scale is also significantly less dense than HGS.

Formation Mechanism of HGS

As noted earlier, hard gray scale or dry scrubber scale forms in zone of high turbulence in reacted alumina handling systems. Fluid bed dribble plates, recycled alumina injectors, reacted alumina transport lines, and reacted alumina delivery lines (especially pneumatic injector tubes) are key areas for scale formation. High turbulence zones act as jet mills that accelerate alumina attrition due to high energy inter-particle collisions. These inter-particle collisions create “new” high energy alumina surfaces, due to fracturing of the SGA particles. These “new” alumina surfaces react instantaneously with atmospheric moisture to re-hydrate (to passivate or reduce surface energy). This “new surface” re-hydration is a vigorously exothermic reaction, causing elevated local surface temperatures on the alumina fines. The energy released by new alumina surface re-hydration is the principal energy driver causing rapid reaction of the surfaces of the SGA superfines and bath superfines to form HGS.

While the reaction mechanism proposed above is logical and is consistent with the data discussed above, no conclusive proof of the reaction mechanism has been offered up to this point in this report. The most compelling proof of the proposed reaction mechanism is being able to synthesize HGS on a lab scale to define the reactants and conditions required to induce HGS formation.

HGS Synthesis

The three key reactive ingredients and one key condition required for formation of HGS are:

- Alumina particles
- Bath fines
- Water
- Inter-particle collisions and particle fracture

The first two ingredients for synthesis of HGS are easily obtained by gathering sampling alumina and bath from smelters. The key condition, a high turbulence “collision” zone, can be simulated by using a sealed 3-ball mechanical grinder.

Varying mixtures of fresh and reacted alumina fines, bath fines and water were placed in a sealed tungsten carbide bench-top ball mill grinder and mixed for 10-20 minutes using three tungsten carbide balls. At the end of each experiment, the temperature of the grinding vessel and the integrity of the ground product were noted.

Alumina and bath fines (no water added) could be ground for any length of time and the reaction product was always a free-flowing well mixed powder. If water was added to this mixture prior to grinding, the temperature of the grinding vessel would increase by

15-20°C and the reaction product was a hard gray scale lining the walls of reaction vessel. By varying the relative proportions of the starting materials, an ideal recipe was identified consisting of 30% bath fines, 55% alumina fines and 15% water.

The elemental composition of lab-synthesized HGS is listed in Table 1 for comparison to that of plant-generated dry scrubber and monovalent scale. The compositional similarity of the synthetic and actual scale samples supports the above listed observation that HGS can be artificially created by co-grinding alumina fines, bath superfines and water.

The superfines created in the reacted alumina stream are key accelerants of HGS formation since they have new sites of outermost surface area available for reaction and are composed of a combination of bath superfines and alumina superfines (ESP dust, attrited alumina and AlF_3 that has spalled off the surface of reacted alumina).

The fact that reacted alumina superfines are enriched in bath superfines and bath fume ($NaAlF_4$) can be inferred by sieving reacted alumina into different particle size fractions and testing each fraction for weight % fluoride content. This relationship is evident from the data shown in Table 2 for samples of reacted alumina collected from a fluid bed dry scrubber. Five separate aliquots of each particle size fraction for reacted alumina were tested for % F. As shown in Table 2, the wt% F of the finest particulate fraction (<325 mesh) is ~3x that of all other size fractions. This step change is due to an increase in bath and fume content of the superfine fraction of reacted alumina.

Table 2. Weight % F data for different particle size fractions of reacted alumina.

Wt % F	Reacted Ore Particle Size Range				
	>150 mesh	150-200 mesh	200-270mesh	270-325mesh	<325mesh
2.35	2.29	2.32	2.24	6.03	
2.25	2.41	2.38	2.3	6.42	
2.19	2.22	2.37	2.25	6.39	
2.2	2.33	2.33	2.27	6.29	
2.16	2.41	2.39	2.26	6.49	
average	2.23	2.332	2.358	2.264	6.324

As noted above, the key ingredients for creating hard gray scale in the ball-mill grinder were alumina fines, bath fines and water. If any of these three ingredients was left out of the mix during grinding, scale was not formed, and the ball mill temperature did not rise rapidly during mixing. It is interesting to note the total moisture content for synthetic HGS in Table 1. Water is vaporized (and lost) during grinding owing to hydrolysis at the new surface area sites and the heat generated by the surface reactions leading to HGS formation.

A common method of removing HGS from reacted alumina transport lines is to remove the pipes from service and simply leave the clogged pipes exposed to the weather for a prolonged period of time. During this time the HGS often becomes fractured and can be broken into pieces by banging on the pipes. This dramatic change in physical properties is due in part to hydration of the HGS while exposed to ambient moisture. As the HGS adsorbs moisture from the air (or rain), it fractures due to internal stresses from unit cell expansion as the AlF_3 converts to $AlF_3 \cdot xH_2O$ and alpha alumina hydrates to Bayerite in the HGS.

How to Minimize HGS Formation

As noted above, there are three key ingredients and one essential condition required for formation of HGS. Any actions that minimize the collective combination of these will inhibit HGS formation. In the section that follows are experience-based examples and commentary on minimizing the formation of HGS. These examples of contributing causes have not been confirmed by experimentation under controlled conditions. They reflect multiple observations in the field across various types of handling and dry scrubbing systems.

Low Pressure Air Supply

Air lift conveyors quite often suffer significant accumulations of HGS in lift tubes, separators and dust collectors. This is very likely due to the effects of high velocity and turbulent flow that will promote inter-particle collisions and attrition in the presence of moisture laden air, fluoride enriched alumina and bath fines.

The capacity of air lifts typically exceeds nominal alumina consumption rates. Typical maximum transport rates of 30% to 50% over nominal consumption are common allowing an opportunity to “catch-up” after maintenance or other outages.

If the air lift nozzle and/or sheaves on the low pressure blower are sized for excessive make-up capacity, consider resizing these elements to move less air. This will reduce the maximum transport rate for the air lift, but this is not entirely undesirable. This change not only lowers the net moisture input by reducing the units of air moved per unit of alumina transported, it also reduces air lift velocity and the attrition of alumina particles.

The net mass of moisture transported to air slide conveyors can also be kept to a minimum with a few simple measures. These include assuring that intake filters are in good condition, are away from sources of rain water, and preferably are under roof.

It is important to avoid the use of compressed air for any transport or feeding of alumina. Unless plant air has a very low dew point, such as -40 C, condensation can enter the system rather easily.

Control of the air flow to air slides is important as well. In some cases targets are neither set nor maintained for lower plenum pressures. These are typically kept at 20” to 25” of water column. Higher flow rates not only introduce a greater flow of moisture, but the greater exhaust rate from the upper plenum can create points of localized velocity that will break particles of alumina.

Particle Attrition

Point-feeders and pot superstructure exhaust systems may be designed such that as much as one-half of superfine particles in the alumina feed stream are drawn into pot ventilation points. This sets up a recirculation loop that multiplies the content of fine particles and some impurities in reacted alumina. It also places superfine particles of alumina that may be high in LOI content on a collision course with dry scrubber components.

Efforts to reduce the amount of superfines delivered to reduction cells or drawn into fume collection systems will also reduce the rate of the formation of HGS. This does not imply that focus

should be placed only on the fine fractions of fresh alumina. Normally the fines and superfines content at the reduction cell far exceed that in the incoming SGA. Attention must also be paid to reducing the generation and the multi-pass recirculation of these fines in the dry scrubbing and reacted alumina handling systems.

There are many steps that can be taken to reduce the amount of superfines that are generated and re-circulated. Some have been reported upon in the literature. [3] The most effective are those that focus on the reduction of the energy that is necessary to break particles of alumina via inter-particle collisions.

Small leaks on systems under negative pressure can do this by creating zones of localized velocity. Small leaks can also draw in moisture, another essential ingredient of HGS.

Over-recirculation of alumina in the dry scrubber will also break particles. A balance must be struck between the HF in the dry scrubber stack and the average number of passes of the alumina through the dry scrubber system.

Steps may also be taken that reduce the recirculation of fine particles in the pot exhaust/reacted alumina loop. Some pot superstructure exhaust system designs include large drop-out zones to prevent many particles from being drawn into the exhaust ducts. A few systems also include cyclonic separation of exhaust system dust. Cyclones are most often used at Söderberg smelters to remove fine particles of carbon residues.

Fluoride Evolution

Reducing the amount of fluoride evolved from the reduction cells lowers the concentration of fluoride on reacted alumina and the amount of atmolite superfines, NaAlF_4 , that are formed.

There is often substantial potential to reduce fluoride evolution by sealing holes in the crust of the reduction cells. The impact of this on fluoride evolution has been described well in the literature. [4]

Placing attention on reducing the amount of time with open holes during anode change also reduce HF evolution.

High excess fluoride content of the bath and/or increases in pot line loads both drive higher evolution of both HF and atmolite especially when bath superheat also increases.

Note that a common practice to follow fluoride evolution, tracking the %F on reacted alumina, can be misleading during periods of rapid accumulation of HGS. Since HGS is rich in fluoride content, often 20% to 30% F, it strips fluoride out of the gas stream as it is formed. Normally this occurs at a low enough rate to be of little consequence.

On occasion an “unexplainable” decrease in %F on reacted alumina and an increase in the consumption of AlF_3 /ton Al produced has been explained by conditions that drove rapid accumulations of HGS. See figures 7a and 7b for an example that illustrates a reduction of %F on reacted alumina and a corresponding increase in AlF_3 consumption at a pre-bake plant.

Cleaning/Removal of HGS Accumulations

As noted earlier HGS formation is something of a chain reaction. As diffuser grates, air lift tubes, alumina conveyance lines and other components accumulate HGS the velocity and turbulence in and around the remaining open area increases. This provides additional energy to cause more inter-particle collisions of alumina. Cleaning out accumulations of HGS is often an essential maintenance step to avoid acute negative impacts on either dry scrubber performance or alumina delivery.

This will translate into inspection and cleaning routines for those elements that are most often impacted by HGS. At some locations this means scheduled cleaning of air lift tubes, use of duty-spares for certain sections of alumina delivery tubes, and cleaning of diffuser plates on a schedule. If a location has problems with HGS waiting for some other maintenance opportunity to come to allow for cleaning is quite often a mistake.

Cleaning methods vary from leaving pipes out in the weather, to banging on pipes to fracture the HGS [and dent the pipes] and even cleaning with high pressure water. There are no fast, easy methods for removal of this scale.

The need for cleaning can also accelerate when conditions change. For example the change of an alumina source, an increase in pot line load, changes in pot crust integrity and increases in pot exhaust rates may all trigger the need to clean key components more often.

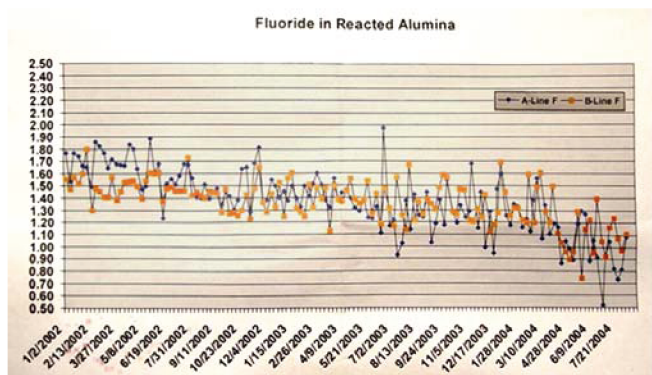


Figure 7a – %F on alumina at a location with an HGS problem

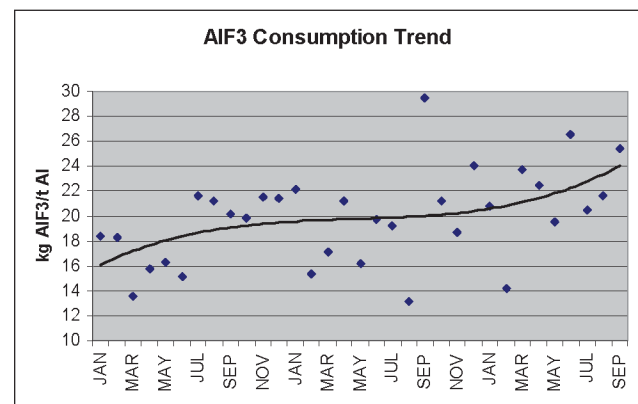


Figure 7b – AlF_3 consumption rate at the same location and time

The focus of all of these examples has been on reducing the content of key ingredients and the essential condition necessary to form HGS. It is noted that in each example that the rate of formation of HGS is reduced, not eliminated. At this time there is no commercially available material or known method that will completely eliminate or prevent the formation of HGS. The best practice is to follow the steps outlined above to control the rate of HGS formation and to remove it with scheduled interventions.

Conclusions

Hard gray scale (HGS) is a term used to describe slate-like scale that forms in all types of pot room dry scrubbers and in downstream alumina-handling system components. HGS is an amorphous reaction product formed from the attrition-induced reaction of bath superfines, alumina superfines and water. HGS formation is greatest in high impact or high attrition areas. The creation of new surface area by the fracture of alumina particles serves as the primary energy source for driving the inter-particle reactions that lead to HGS formation.

There is no material or method that prevents the formation of HGS in commercial use. However, systems that also draw pitch volatile matter such as the exhaust from Söderberg cells or anode baking furnaces are much less likely to have issues with HGS.

There are methods that can be used to reduce and control the rate of HGS formation. These are already in practical application at numerous smelting locations.

As the industry moves toward higher line loads, higher pot evacuation velocities, and away from the use of technologies such as fluid-bed scrubbers it is reasonable to expect an increased rate of HGS formation in dry scrubbers and reacted alumina transport lines.

This may become positively or negatively accentuated by shifts in alumina properties that affect the content of fines and superfines or the ability of alumina particles to resist breakage.

This inevitability accentuates the need implement deliberate measures to reduce HGS formation at existing smelters. It also establishes something of a “pay me now or pay me later” scenario for new smelting projects. The choice is to use up-front capital to build systems that are less susceptible to the negative impacts of HGS and less likely to form HGS at a rapid rate or to face those factors that are steadily increasing HGS-induced issues and recurring maintenance costs over the life of the smelter.

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