

Water-Formed and Steam-Formed Deposits

Locations

Deposits can occur anywhere water or steam is present in a boiler. While wall and screen tubes are usually the most heavily fouled, roof and floor tubes often contain deposits as well. Superheaters and reheaters frequently contain deposits that are formed elsewhere and are carried into the systems with boiler water. Steam is not often generated in economizers. Deposits in these tubes are usually made up of corrosion products moved from their origination sites.

Deposition can be substantial during steam generation. Tube orientation can influence the location and amount of deposition. Deposits are usually heaviest on the hot side of steam-generating tubes. Because of steam channeling, accumulations are often heavier on top portions of horizontal and slanted tubes. Also, deposition often occurs immediately downstream from circumferential-weld backing rings, which disturb flow and are favored sites for steam blanketing. Because deposits tend to concentrate in the hottest regions of steam-generator tubes, those tubes near the bottom rear wall of boilers using chain-grate stokers, and screen tubes

are susceptible to deposition. Coarse particulate matter is likely to be found in horizontal runs and where flow velocity is small.

Most economizers are designed to operate without producing steam. Waterborne deposits usually enter the economizer from sources such as the returned condensate (usually not polished). Oxides formed as a result of elevated oxygen concentrations prior to or inside the economizer may be moved and deposited in the economizer.

Mud and steam drums often contain deposits. Because drums are readily accessible, a visual inspection can provide many details about water chemistry and deposition processes. For example, sparkling black magnetite crystals may precipitate in steam drums when iron is released by the decomposition of organic complexing agents.

Superheater deposits are caused by carryover of boiler water, sometimes associated with foaming or high water levels. Such deposits will usually be concentrated near the superheater inlet or in nearby pendant U-bends. Contaminated attemperation water can also add deposits immediately downstream from the introduction point. Chip scale and exfoliated oxide particles can be blown through the superheater, accumulating in pendant U-bends, or even more seriously, can be carried into turbines.

General Description

The term *deposits* refers to materials that originate elsewhere and are conveyed to a deposition site. Deposits cannot be defined as corrosion products formed in place, although corrosion products formed elsewhere and then deposited do qualify. Oxides formed from boiler metal are not deposits unless they have been moved from their origination sites. *This distinction is fundamental.*

Boiler deposits come from four sources: water borne minerals, treatment chemicals, corrosion products (preboiler and boiler), and contaminants. Deposits from these sources may interact to increase deposition rates, to produce a more tenacious layer, and to serve as nucleation sites for deposit formation. Such species include (but are not limited to) metal oxides, copper, phosphates, carbonates, silicates, sulfates, and contaminants, as well as a variety of organic and inorganic compounds.

One deposition process involves the concentration of soluble and insoluble species in a thin film bordering the metal surface during steam-bubble formation (Fig. 1.1). Material segregates at the steam/water interface, moves along the interface, and is deposited at the bubble base as the bubble grows. Other deposit mechanisms involve precipitation from solution and settling of large particulate matter. Inverse-temperature solubility leads to deposition where heat transfer is great.

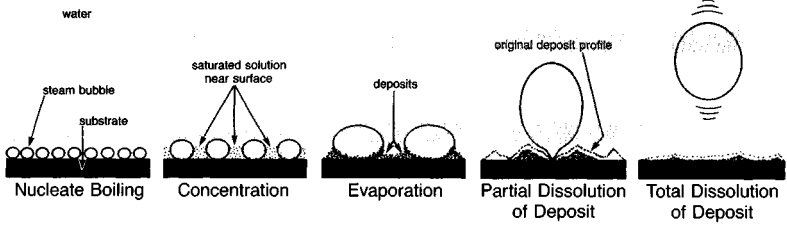


Figure 1.1 Five instants in the life of a steam bubble.

The tendency to form deposits is related to localized heat input, water turbulence, and water composition at or near the tube wall. When a steam bubble becomes dislodged from a tube wall, the deposits are washed with water. The rate at which the deposit builds depends on the rate of bubble formation and the effective solubility of the deposit. In cases of high heat input, a stable steam blanket can form and cause concentration of water-soluble material (Fig. 1.2). Steam-blanket deposits do not redissolve, because the surface cannot be washed while blanketed with steam (Fig. 1.3). Steam blanketing also results from surface irregularities, which disturb water flow. Downstream of such irregularities, low-pressure areas are formed, favoring steam buildup and consequently deposit formation.

Steaming does not often occur in economizers. Deposits are usually iron-rich. The iron oxide is produced in the preboiler system or is formed in the economizer itself (Figs. 1.4 and 1.5).

Thermal stresses aid oxide spalling. Exfoliation of thermally formed oxides in superheaters and reheaters can cause accumulation of oxide

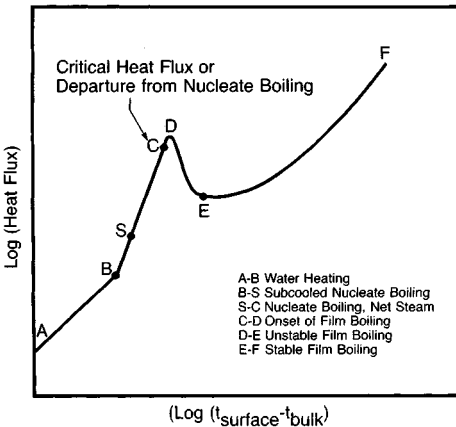


Figure 1.2 Heat transfer to water and steam in a heated flow channel. Relation of heat flux to temperature difference between channel-wall and bulk-water or steam temperature. (Courtesy Babcock and Wilcox Company, Steam/Its Generation and Use, New York, 1972).

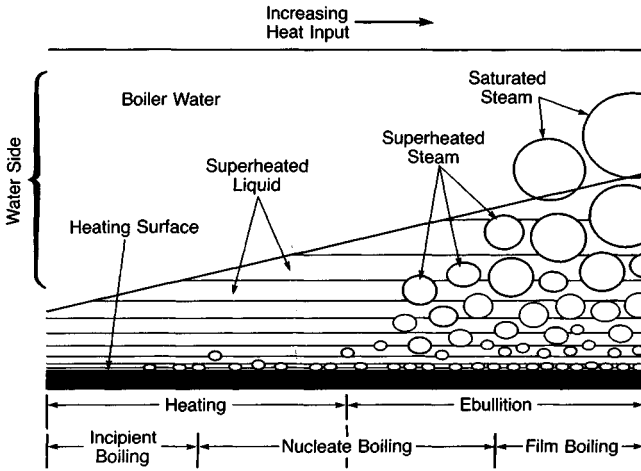


Figure 1.3 Transition from heating to boiling (ebullition) as wall temperature increases.

chips in U-bends and long horizontal runs (Figs. 1.6 and 1.7). Scaling temperatures (the temperatures above which oxide formation is rapid) for a variety of alloys are shown in Table 2.1. Waterborne deposits can also accumulate because of carryover due to foaming, “gulping,” and water washing. Steam-soluble species can be carried through superheaters and



Figure 1.4 Thick layer of friable iron oxide in an economizer tube. Most iron was carried into the economizer from the preboiler system.



Figure 1.5 Fragmented hematite layer on an internal surface of an economizer. Most oxide was formed in place, but some was moved as fragments and chips.

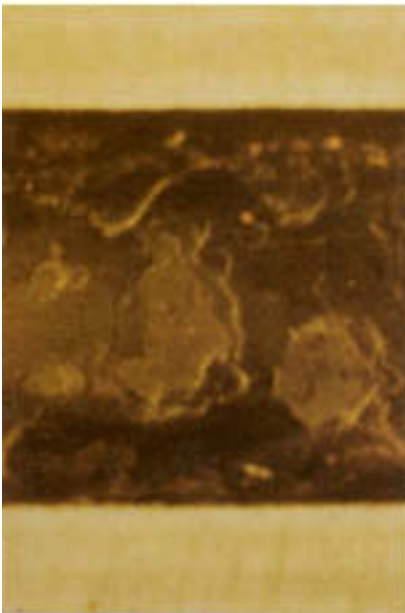


Figure 1.6 Exfoliated magnetite patches in a tube from the primary superheater of a utility boiler. Magnetite chips can be carried into turbines and cause severe damage (see Fig. 1.7).



Figure 1.7 Fine-mesh turbine inlet screen. Pieces of exfoliated oxide from superheater tubing are wedged into screen openings. (Magnification: 7.5 \times .)

deposited on turbines. If chlorides and sulfates are present, hydration can cause severe corrosion due to hydrolysis (Figs. 1.8 and 1.9).

Critical Factors

The rate at which deposits form on heat-transfer surfaces is controlled mainly by the solubility and physical tenacity of the deposit and the amount of water washing that occurs where steam is generated. Solubility,



Figure 1.8 Severely corroded blades from high-pressure condensing stage of a turbine. Deposits were removed to reveal attack.

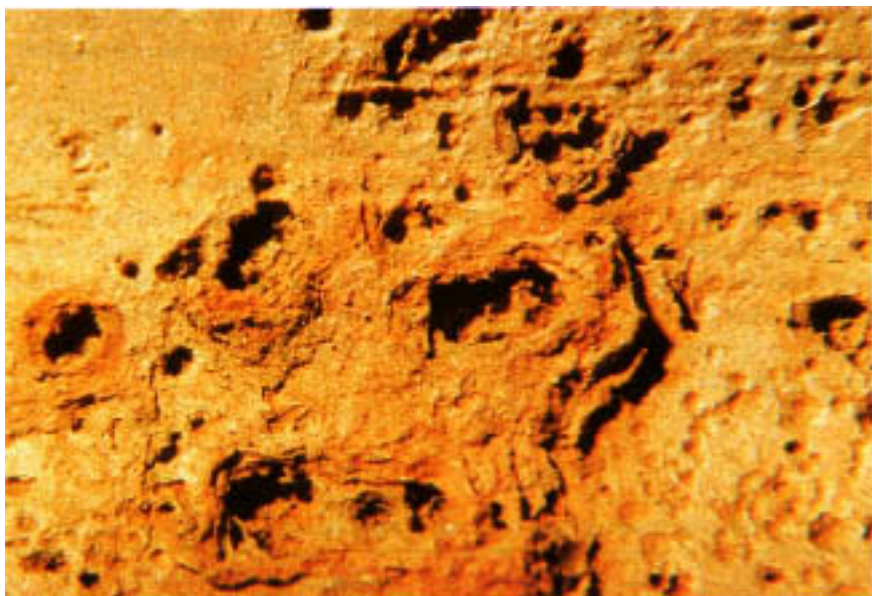


Figure 1.9 Deposits on turbine blades before cleaning, as in Fig. 1.8. (Magnification: 7.5 \times .)

tenacity, and water washing, in turn, depend on other factors such as dissolved-solids concentration, formation temperature, agglomeration morphology, and turbulence. However, the prerequisite factor for significant deposit formation is usually steam formation. In fact, deposits can form even when steaming is slight (Fig. 1.10). As long as nucleate boiling is



Figure 1.10 Tube sections virtually plugged with deposits. The tube on the right is from a low-pressure boiler and is fouled with almost pure calcium carbonate. The center tube contains silicates, phosphates, and other compounds; fouling occurred on standby service. The section on the left is reddened by almost 20% elemental copper. Such heavy deposition can occur only when internal pressures are low. Otherwise rupture would occur.

occurring, heat transfer is controlled by tube-wall and deposit thermal conductivities and by the gas-side temperature. The thermal conductivities of several boiler deposits and alloys are given in Table 1.1.

Salts having inverse-temperature solubility deposit readily on heat-transfer surfaces. For example, calcium sulfate and calcium phosphate deposit preferentially in hot areas as temperatures increase. Eventually steam blanketing occurs and evaporation to dryness causes concentration of species having normal-temperature solubility (Fig. 1.11). Frequently, the deposits of the most insoluble materials are found in water-cooled tubes having the highest heat transfer, such as screen tubes. When evaporation to dryness occurs, both soluble and insoluble deposits are usually found together.

TABLE 1.1 Thermal Conductivities (ϵ) of Alloys and Deposits

	Thermal conductivity	
	$W/(m^2 \cdot ^\circ C)$	$(Btu \cdot ft.)/(h \cdot ft^2 \cdot ^\circ F)$
<i>Alloys</i>		
304 Stainless	22(500°C), 16(1000°)	12.5(932°F), 9.4(212°F)
410 Stainless	28(400°C), 25(1000°C)	16.1(752°F), 14.4(212°F)
Alloy steel (0.34 C, 0.55 Mn, 0.78 Cr, 3.53 Ni, 0.39 Mo, 0.05 Cu)	36*	21*
Copper	420*	240*
Carbon steel (0.23 C, 0.64 Mn)	55*	32*
Aluminum	235*	136*
<i>Deposits</i>		
Aluminum oxide, fused (Al_2O_3)	3.60	2.1
Analcite ($Na_2O \cdot Al_2O_3 \cdot$ $4SiO_3 \cdot 2H_2O$)	0.19	0.76
Calcium carbonate ($CaCO_3$)	0.14	0.56
Calcium phosphate [$Ca_3(PO_4)_2$]	0.55	2.20
Calcium sulfate ($CaSO_4$)	0.21	0.83
Ferric oxide (Fe_2O_3)	0.09	0.35
Magnesium oxide (MgO)	0.17	0.69
Magnesium phosphate [$Mg_3(PO_4)_2$]	0.33	1.30
Magnetite (Fe_3O_4)	0.45	1.8
Porous materials	0.01	0.06
Quartz (SiO_2)	0.24	0.97
Serpentine ($3MgO \cdot$ $2SiO_2 \cdot 2H_2O$)	0.16	0.63

* Room temperature.

NOTE: $(Btu \cdot ft.)/(h \cdot ft^2 \cdot ^\circ F) = 1.73 W/(m^2 \cdot ^\circ C)$



Figure 1.11 Sodium hydroxide-rich deposit on fire side of wall tube from 600-psi boiler. Note the bulge due to long-term overheating.

Even a relatively small amount of deposit can cause wall temperatures to rise considerably. As wall temperature rises, the tendency to steam-blanket increases (Fig. 1.3). Blanketing decreases heat flow, potentially causing overheating and rupture (see Chap. 2, “Long-Term Overheating”).

Water quality also has a significant influence on deposition. Suggested acceptable feedwater quality as a function of boiler pressure is shown in Table 1.2. This table indicates that fewer contaminants can be tolerated at high boiler pressures. The insulating effects of deposits become less tolerable as pressures rise, because overheating is more likely. Maximum acceptable concentrations of boiler-water salines are shown in Table 1.3. The recommended dissolved solids decrease by a factor of 100 when pressure rises from 100 psi (0.69 MPa) to 2000 psi (13.8 MPa). Allowable silica levels decrease by a factor of 250 and suspended solids by a factor of 500.

A rule of thumb concerning tube cleanliness suggests that high-pressure boilers (pressures greater than 1800 psi or 12.4 MPa) are considered relatively clean if less than 15 mg/cm^2 ($\sim 14 \text{ g/ft}^2$) of deposits are present on water-cooled tubes. This amount of deposit is typical of almost all kinds of clean boilers, regardless of water chemistry, boiler type, or fuel. In some boilers, porous magnetite layers up to 11 mg/cm^2 (10 g/ft^2) produce no significant impairment of heat transfer. Moderately dirty boiler tubes

TABLE 1.2 Recommended Feedwater Quality

Pressure (psi)	Silica range (ppm)	Total hardness	Maximum (ppm)		
			Oxygen	Iron*	Copper*
100	15–25	75.00	—	—	—
200	10–20	20.00	—	—	—
300	7.5–15	2.00	—	—	—
500	2.5–5.0	2.00	0.030	—	—
600	1.3–2.5	0.20	0.030	—	—
750	1.3–2.5	0.10	0.030	0.050	0.020
900	0.8–1.5	0.05	0.007	0.020	0.015
1000	0.2–0.3	0.05	0.007	0.020	0.015
1500	0.3 max	0.00	0.005	0.010	0.010
2000	0.1 max	0.00	0.005	0.010	0.010
2500	0.05 max	0.00	0.003	0.003	0.002
3200+	0.02 max	0.00	0.002	0.002	0.001

* In modern industrial boilers, which have extremely high rates of heat transfer, these concentrations should be essentially zero. Similarly, total hardness should not exceed 0.3 ppm CaCO_3 , even at the lower pressures; suspended solids in the feedwater should be zero if possible.

SOURCE: Courtesy of Chemical Publishing Company, *The Chemical Treatment of Boiler Water*, James W. McCoy, New York, 1981.

NOTE: 1 psi = 0.006895 MPa

contain 15 to 40 mg/cm² (14 to 37 g/ft²) of deposits, and boiler tubes containing more than 40 mg/cm² (37 g/ft²) are considered very dirty. Guidelines for high-pressure boilers are listed in Table 1.4. Heat transfer is severely reduced when deposit loading becomes excessive. One large boiler manufacturer recommends boiler cleaning at 32 mg/cm² (30 g/ft²) for lower-pressure boilers. Prolonged operation above the maximum deposit loadings may produce serious corrosion and overheating failures. However, the weight of deposits alone does not always accurately indicate the tendency to overheat. Deposit composition and morphology also influence heat transfer.

Identification

Boiler treatment chemicals, feedwater composition, and heat input affect deposition. At pressures of 2500 psi (17.2 MPa) or more, hydrazine is normally used. Demineralization and condensate polishing are other commonly used water-treatment practices. This means deposits are likely to contain only iron oxide produced by the corrosion of internal surfaces, and possibly copper, nickel, or other metals and contaminants (Fig. 1.12); no water-treatment chemicals or their reaction products will normally be found. At lower pressures, a variety of species can occur. Typical com-

TABLE 1.3 Recommended Concentration of Boiler Salines

Pressure (psi)	Saturation temperature (°F)	Maximum (ppm)						Range (ppm)		
		Dissolved solids	Suspended solids*	Total alkalinity†	Silica	Sludge conditioners		Residual phosphate	Residual sulfite	Residual hydrazine
						Natural	Synthetic			
100	328	5000.00	500	900	250.00	150	15	NR‡	90-100	NR
200	382	4000.00	350	800	200.00	150	15	40-50	80-90	NR
300	417	3500.00	300	700	175.00	100	15	30-40	60-70	NR
500	467	3000.00	60	600	40.00	70	15	25-30	45-60	NR
600	486	2500.00	50	500	35.00	70	10	20-25	30-45	NR
750	510	2000.00	40	300	30.00	NR	10	15-20	25-30	NR
900	532	1000.00	20	200	20.00	NR	5	10-15	15-20	0.10-0.15
1000	545	500.00	10	50	10.00	NR	3	5-10	NR	0.10-0.15
1500	596	150.00	3	0	3.00	NR	NR	3-6	NR	0.05-0.10
2000	636	50.00	1	0	1.00	NR	NR	1-3	NR	0.05-0.10
2500	668	10.00	0	0	0.50	NR	NR	NR	NR	0.02-0.03
3200‡	705	0.02	0	0	0.02	NR	NR	NR	NR	0.01-0.02

* Guidelines for pressures from 100 to 900 psi apply to conventional field-erected boilers with moderate rates of heat transfer, say 50,000 Btu/(ft² · h). At high rates characteristic of packaged boilers, large amounts of insoluble material cannot be managed effectively by a dispersant presently available.

† Zero alkalinity refers to hydroxide ion, i.e., Pa and M alkalinites (2P-M). There is always some alkalinity produced by ammonia, hydrazine, morpholine, or other bases.

‡ NR = not recommended.

SOURCE: Chemical Publishing Company, *The Chemical Treatment of Boiler Water*, James W. McCoy, New York, 1981.

TABLE 1.4 Boiler-Tube Cleanliness

Boiler type	Deposits (mg/cm ²)		
	Clean	Moderately dirty	Very dirty
Supercritical units	<15	15–25	>25
Subcritical units (1800 psi and higher)	<15	15–40	>40

NOTE: 1 mg/cm² ~ 1 g/ft².
1 psi = 0.006895 MPa

SOURCE: K. L. Atwood, and G. L. Hale, *A Method for Determining Need for Chemical Cleaning of High-Pressure Boilers*, presented to American Power Conference, Chicago, Illinois, April 20–22, 1971.

pounds, and their likely locations and deposit characteristics can be found in Table 1.5.

Iron oxides

A smooth, black, tenacious, dense magnetite layer naturally grows on steel under reducing conditions found on boiler water-side surfaces (Fig. 1.13). Magnetite forms by direct reaction of water with the tube metal. In higher-pressure boilers, the magnetite contains two layers, which ordinarily can be seen only by microscopic examination. Particulate iron oxide can deposit on top of the smooth, thermally formed magnetite layer if settling rates are high and/or if steaming is appreciable (Fig. 1.14). Usually, coarse, particulate magnetite will not tenaciously adhere to surfaces unless intermixed with other deposits. Sparkling, black, highly crystalline magnetite needles will often be present near caustic corrosion sites. Similar magnetite crystals can sometimes produce a sparkling surface coating on steam

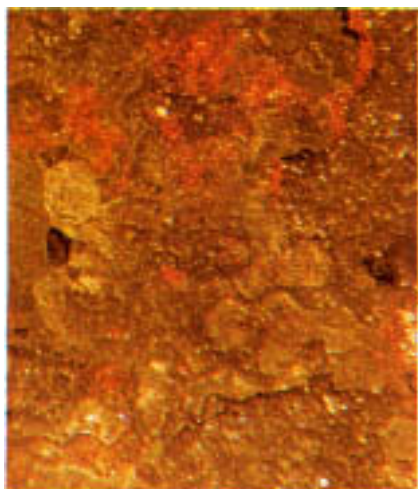


Figure 1.12 Elemental copper on wall tube from a high-pressure utility boiler.



Figure 1.13 Smooth, tenacious, black, magnetite layer on a well-protected boiler tube.

drums and tubes (Fig. 1.15 and 1.16). Scraping small amounts of this material from surfaces and exposing these particles to a magnet usually indicates whether iron is present.

Hematite formation, on the other hand, is favored at somewhat lower temperatures and higher oxygen concentrations. Hematite is a binder species that tends to accumulate and hold other materials in the deposit. Hematite can be red if formed where oxygen concentrations are high. Hematite usually is present in economizers in conjunction with oxygen corrosion (Fig. 1.5).

Other metals and their oxides

Copper is deposited either by direct exchange with iron or by reduction of copper oxide by hydrogen evolved during corrosion. It is common to see large, reddish stains of elemental copper intermixed with corrosion products such as magnetite and hematite near caustic corrosion sites because of the hydrogen generation associated with attack (Fig. 1.12). The reddish color superficially resembles hematite. Elemental copper can be easily discriminated from other material by a silver nitrate test. A single drop of silver nitrate will precipitate white silver crystals almost immediately if elemental copper is present. Copper oxide formed under boiler conditions is black and nonmagnetic. Galvanic corrosion associated with copper deposits (either elemental copper or oxide) is exceedingly rare in well-passivated boilers.

Zinc and nickel oxides will sometimes be found in conjunction with copper deposits. This is to be expected, since zinc and nickel are often

TABLE 1.5 Components of Water-Formed Deposits

Mineral	Formula	Nature of deposit	Usual location and form
Acmite	$\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$	Hard, adherent	Tube scale under hydroxyapatite or serpentine
Alpha quartz	SiO_2	Hard, adherent	Turbine blades, mud drum, tube scale
Amphibole	$\text{MgO} \cdot \text{SiO}_2$	Adherent binder	Tube scale and sludge
Analcite	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Hard, adherent	Tube scale under hydroxyapatite or serpentine
Anhydrite	CaSO_4	Hard, adherent	Tube scale, generating tubes
Aragonite	CaCO_3	Hard, adherent	Tube scale, feed lines, sludge
Brucite	$\text{Mg}(\text{OH})_2$	Flocculant	Sludge in mud drum and waterwall headers
Copper	Cu	Electroplated layer	Boiler tubes and turbine blades
Cuprite	Cu_2O	Adherent layer	Turbine blades, boiler deposits
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Hard, adherent	Tube scale, generating tubes
Hematite	Fe_2O_3	Binder	Throughout boiler
Hydroxyapatite	$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	Flocculant	Mud drum, waterwalls, sludge
Magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_6$	Adherent binder	Tubes, mud drum, waterwalls
Magnetite	Fe_3O_4	Protective film	All internal surfaces
Noselite	$3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{Na}_2\text{SO}_4$	Hard, adherent	Tube scale
Pectolite	$\text{Na}_2\text{O} \cdot 4\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$	Hard, adherent	Tube scale
Serpentine	$3\text{MgO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$	Flocculant	Sludge
Sodalite	$3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{NaCl}$	Hard, adherent	Tube scale
Xonotlite	$5\text{CaO} \cdot 5\text{SiO}_2 \cdot \text{H}_2\text{O}$	Hard, adherent	Tube scale

SOURCE: Courtesy of Chemical Publishing Company, *The Chemical Treatment of Boiler Water*, James W. McCoy, New York, 1981.



Figure 1.14 Spots of particulate iron oxide deposit mirroring stud locations on a wall tube of a recovery boiler. The studs, if exposed, concentrate heat, causing higher rates of steam generation and deposition. Note the white deposits of sodium hydroxide encircling each powdery magnetite spot.



Figure 1.15 Sparkling black magnetite crystals on internal surface of a wall tube. Crystals are formed by precipitation on surfaces, or are transported from preboiler areas.



Figure 1.16 Patch of sparkling magnetite crystals associated with caustic corrosion site. Such crystals are often found near sites of acid and caustic corrosion.

present in brass and cupronickels used in condensers and feedwater heaters. Usually, these elements are deposited at lower concentrations than copper. Nickel oxide has been indicated as a “binder” compound promoting tenacious deposition. However, nickel is usually present in relatively low concentrations and can be detected by chemical analysis using *x*-ray fluorescence or diffraction.

Salts

The least soluble compounds deposit first when boiling occurs. Calcium carbonate deposits quickly, forming a white, friable deposit that will effervesce when exposed to hydrochloric acid (Fig. 1.17). Calcium sulfate requires a higher degree of concentration to deposit than carbonate. The presence of phosphates can sometimes be inferred by friable (but less so than calcium carbonate) deposits.

Magnesium phosphate is a binder that can produce very hard, adherent deposits. Most magnesium phosphate deposits are colorless but become red, brown, or black when contaminated with iron oxides.

Insoluble silicates are present in many boilers. Many silicates are very hard and are almost insoluble in acids except for hydrofluoric. Complex silicates such as analcite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), acmite



Figure 1.17 Calcium carbonate deposit (see Fig. 1.10).



Figure 1.18 Analcite formed by carryover of alum from clarifiers. Note how the deposit has spalled from the bulge.

($\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$), or sodalite [$\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{NaCl}$] can be evidence for steam blanketing, since intermediate sodium compounds are soluble. Analcite frequently forms if alum is carried over from clarifiers (Fig. 1.18).

In general, water-soluble deposits can be retained only if localized concentration mechanisms are severe. Therefore, the presence of species such as sodium hydroxide, sodium phosphate, and sodium sulfate should be considered proof of evaporation to dryness. It has been reported that the strong odor of hydrogen sulfide due to sulfite decomposition was detected near a boiler where hot spots were present.

Hydrolyzable salts such as MgCl can gain entrance to boiler water through leaks in seawater condensers. Chlorides will concentrate in porous deposits and hydrolyze to form hydrochloric acid. Decomposition of oil, grease, and other organic contaminants can also produce acid conditions.

Deposit morphology

Much of the preceding discussion involves the identification of deposits based only on individual chemical natures. However, most real boiler deposits contain many intermixed compounds. The deposit morphology can influence the species which are found and also gives clues as to the heat input, water conditions, and corrosion mechanisms under which they were formed.

Any deposit that resists rinsing is especially undesirable. In particular, insoluble, permeable deposits such as coarse particulate matter are harmful. They permit the concentration of more soluble species in their pores. Hence, sodium hydroxide may be found intermixed with porous, insoluble species. Deposition of the porous species often predates the concentration of the more soluble species.

In general, the older the deposit, the harder it is and the more tenaciously it adheres to tube walls. As deposits age, they fill their interstices with solid material, resulting in increased bulk, density, and hardness. There are exceptions to this rule, and these judgments are naturally somewhat subjective. Nevertheless, the presence of hard, tenacious deposits often indicates that deposition has been occurring for a long time at high metal temperatures.

Deposit stratification indicates changes in water chemistry, heat input, etc. It is often possible to identify deposits formed during different water-treatment programs through careful inspection and analysis of laminate scales. The order in which the deposits appear usually can provide a chronological deposition history.

Elimination

All deposits are undesirable and ultimately result from water-chemistry properties or boiler operations practices. Proper water treatment can reduce deposition. The general rules of proper water treatment are obvious. Water-chemistry upsets and operation changes should be minimized.

Deposition can be avoided by operating at or slightly below design loads and ensuring that all boiler components are functioning properly. The most important boiler operating characteristic influencing deposition is firing practice. Also, elimination of hot spots, correct monitoring of water levels, and maintenance of a constant load are necessary to avoid deposition. In addition, correct burner position, well-considered fuel adjustments, and appropriate blowdown practices contribute to reduced deposition.

Cautions

Deposits rarely contain only a single compound. Chemical analysis is often necessary to determine the amount and variety of each chemical species. Soluble species will be washed away when the boiler cools and steam generation ceases. Washing sometimes results in laboratory analysis that does not accurately reflect in-service compositions. It is usually safe to assume that concentrations of highly soluble species are underreported in laboratory analysis. The presence of any highly soluble material is usually sufficient to prove deviations from nucleate boiling.

The amount, composition, and stratification of deposits are often altered near a rupture site. Escaping fluids may remove deposits near the rupture. Occasionally, fire-side combustion products may find their way onto internal surfaces near the rupture. Weight determinations for deposits near bulged or ruptured surfaces are usually underestimates of actual in-service values.

Corrosion products can be confused with deposits. This is especially true in superheaters suffering idle-time oxygen corrosion, where tubercular growth is often confused with carryover of boiler-water solids (see Chap. 8, "Oxygen Corrosion"). Magnetite needles associated with low-pH excursions can also be confused with particulate iron brought in from the pre-boiler system.

Related Problems

See also Chap. 2, "Long-Term Overheating"; Chap. 3, "Short-Term Overheating"; Chap. 4, "Caustic Corrosion"; Chap. 6, "Low-pH Corrosion during Service"; Chap. 7, "Low-pH Corrosion during Acid Cleaning"; and Chap. 8, "Oxygen Corrosion."

CASE HISTORY 1.1

Industry:	Pulp and paper
Specimen Location:	Economizer tube from recovery boiler near upper header
Orientation of Specimen:	Curved (horizontal to vertical—J-shaped)
Years in Service:	10
Water-Treatment Program:	Chelant
Drum Pressure:	600 psi (4.13 MPa); feedwater pressure, 820 psi (5.65 MPa)
Tube Specifications:	2 in. outer diameter
Fuel:	Black liquor

During removal of failed economizer tubes, heavy internal deposits were found unexpectedly. Internal surfaces of some economizer tubes were partially lined with an irregular layer of soft, flaky iron oxide. Underlying oxides were black. A 1-in.-thick layer of friable material accumulated at the tube bend is shown in Fig. 1.19. Close observation revealed that the accumulated material consisted of anthracite particles and resin beads (Fig. 1.20). The deposit had been transported from a disintegrated resin bed. The metal surface beneath the deposit was gouged and thinned.

The accumulated deposit retarded coolant flow, yet overheating could not occur because flue-gas temperatures were too low (about 550°F, or 288°C). Deviations from nucleate boiling beneath the deposit did occur, leading to concentration of sodium hydroxide and associated corrosion (see Chap. 4, “Caustic Corrosion”).

It is extraordinary that this deposit did not cause failure. Rather, other



Figure 1.19 Anthracite and resin beads beneath a stratified iron oxide layer.



Figure 1.20 Anthracite and resin beads. (Magnification: 7.5 \times .)

nearby tubes failed as a result of erosion from external surfaces and oxygen corrosion. At this time the deposits were discovered.

The resin-bed disintegration was not found until the economizer deposits were found. Although these deposits must have been carried into other parts of the boiler, no failures were traced to their presence.

CASE HISTORY 1.2

Industry:	Pulp and paper
Specimen Location:	Superheater outlet
Orientation of Specimen:	Vertical (stub end down)
Years in Service:	3½
Water-Treatment Program:	Phosphate
Drum Pressure:	900 psi
Tube Specifications:	2 in. (5.1 cm) outer diameter, stub-end, low-alloy steel (1½% Cr)
Fuel:	Coal

A 2-ft section of superheater-tubing stub end was plugged solid with deposits that were still soaked with water when the tube was split. Sections were gently heated for 3 days to dry the deposit in situ. After drying, white deposits became visible at the end of the stub (the lowest tube point in service) (Fig. 1.21).

The tube contained about 2 lb of deposit for every 2 in. (5.1 cm) of its length. Away from the stub end, the deposit contained about 80% magnetite



Figure 1.21 Longitudinally split stub end from a superheater outlet. The tube is plugged with deposits. The white material is sodium hydroxide and sodium carbonate concentrated at the bottom of the stub end. The black material is mostly magnetite.

and 7% sodium hydroxide and sodium carbonate by weight. Small amounts of sulfur, chlorine, phosphorus, chromium, and manganese were also detected. At the stub end, about half the deposit was sodium hydroxide and sodium carbonate.

Deposits were caused by chronic contamination of attemperation water and/or carryover of boiler water into the superheater header from the steam drum. Water was converted to steam and left solids behind. Solids accumulated during a considerable period in stagnant, low-flow regions like stub ends.

The color difference between deposits at the stub end and shank indicates segregation of the soluble white alkaline material to the lowest portion of the stub. Segregation is caused by percolation of solute-rich water to the stub end. The fact that the white material was concentrated at the bottom of the tube after drying supports this conclusion.

Cleaning these stub ends is a very difficult task. However, cleaning or removal of the ends is necessary to prevent caustic corrosion and overheating.

CASE HISTORY 1.3

Industry:	Pulp and paper
Specimen Location:	Crossover tube
Orientation of Specimen:	Horizontal
Years in Service:	20
Water-Treatment Program:	Phosphate
Drum Pressure:	800 psi (5.52 MPa)
Tube Specifications:	2½ in. (6.4 cm) outer diameter
Fuel:	Black liquor and fuel oil

The crossover tube contained a small bulge and rupture. A white, friable deposit layer having a density of 16 g/ft² (17 mg/cm²) was present on hot-side internal surfaces; 1 g/ft² was present on the cold side. Deposits were bounded on both sides by sharp borders (Fig. 1.22). The borders indicate the steam-blanketing terminus. Deposition took place during a brief episode of high fire-side heat input. High heat input resulted in overheating and eventual failure.



Figure 1.22 Deposit layer on the internal surface of the hot side of a crossover tube. Some deposit spalled off at a shallow bulge. Note the sharp boundaries indicating the terminus of steam blanketing.

Deposits consist of basic calcium phosphate (hydroxyapatite), sodium aluminum silicate hydrate, magnetite, magnesium silicate, and small amounts of other materials. Some alum was carried over from clarifiers. Firing practices and water clarification were reviewed and changed appropriately.

CASE HISTORY 1.4

Industry:	Pulp and paper
Specimen Location:	Primary superheater, pendant U-bend
Orientation of Specimen:	Vertical
Years in Service:	11
Water-Treatment Program:	Phosphate
Drum Pressure:	1250 psi (8.62 MPa)
Tube Specifications:	1¾ in. (4.45 cm) outer diameter; 2¼% Cr, 1% Mo
Fuel:	Hog fuel and coal

A pendant U-bend section of the superheater was removed from service because of fire-side metal loss associated with slagging. When the internal surface was examined, severe blistering of the magnetite layer was found (Fig. 1.23). Spalling of the magnetite layer had occurred. Although such spalling can lead to turbine erosion, none was detected.

Oxide spalling (exfoliation) is caused by fluctuating stresses, usually

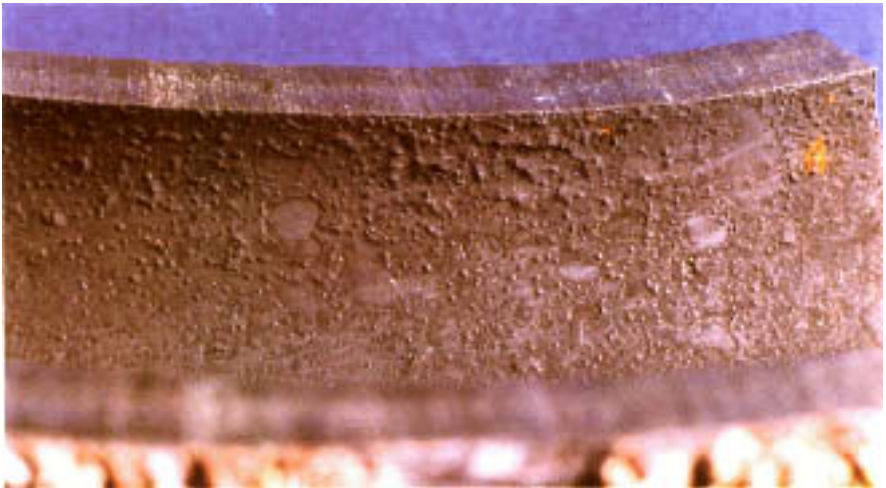


Figure 1.23 Magnetite blisters on the internal surface of a U-bend in a primary superheater. Note that the magnetite has spalled in places.

fluctuating thermal stresses. Stresses can become large when tubes are slagged. Furnace-gas channeling and "laning" can produce hot spots. The fracturing of slag, perhaps during soot blowing, can cause rapid surface-temperature variations. It is not established that soot blowing alone can cause exfoliation.

Magnetite bubbles grow because the thermally formed magnetite occupies a larger volume than the metal from which it forms. Therefore, compressive stresses may occur in the growing layer, tending to cause buckling. When temperatures are high, the oxide may slowly deform instead of fracturing.

Virtually all superheaters experience some magnetite exfoliation as they age. However, slagging, large load swings, mechanical vibration, and frequent up-and-down operation accelerate the stresses leading to exfoliation.

CASE HISTORY 1.5

Industry:	Utility
Specimen Location:	Fine turbine screen
Orientation of Specimen:	Vertical
Years in Service:	8
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	2200 psi (15.2 MPa)
Sample Specifications:	0.035-in. (0.088-cm) mild steel wire; screen-opening size of 0.040 in. (0.012 cm)
Fuel:	Coal

After routine superheater inspections, it was revealed that spalling and exfoliation of magnetite on internal surfaces had occurred. Sections of both coarse and fine turbine-inlet screens were removed for inspection.

Approximately 10% of the fine screen openings were plugged with magnetite chip scale. Small exfoliated chips had been blown through the superheaters and had lodged in the screen (Fig. 1.7). A few rocks and cutting-torch spatter beads were also trapped. The coarse screen caught magnetite chips as thick as 0.010 in. (0.025 cm) and as wide as 0.15 in. (0.038 cm). The side of the coarse screen facing steam flow was hammered and peened by impact with flying projectiles.

A slight decrease in turbine efficiency had been noticed recently, and it was suspected that hard-particle erosion from exfoliated oxide might be damaging buckets. Subsequent turbine inspections revealed only minor damage.

Chemical treatments to reduce slagging were suggested, and soot-blowing practices were reviewed. Chemical cleaning of the superheater was deemed unnecessary at the time.

CASE HISTORY 1.6

Industry:	Chemical plant
Specimen Location:	Target-wall tube, 6 ft (1.8 m) above lower-wall header
Orientation of Specimen:	Horizontal
Years in Service:	5
Water-Treatment Program:	Polymer
Drum Pressure:	425 psi (2.93 MPa)
Tube Specifications:	3¼ in. (8.26 cm) outer diameter
Fuel:	Natural gas and No. 6 fuel oil

One of the seventy-four target-wall tubes was bulged and ruptured. A thick, friable, tan deposit layer covered the internal surface (Fig. 1.24). The hot-side deposit weight was 100 g/ft², while the cold-side weight was 82 g/ft². Deposits contained calcium carbonate, calcium silicate, calcium phosphate, and magnesium silicate hydroxide.

The boiler was fired intermittently at up to 90,000 pounds (40,900 kilograms) of steam per hour for over 1 year [design was 75,000 lb/h (34,000



Figure 1.24 Cross section of bulged target-wall tube. Deposits are heavy on both hot and cold sides. Most deposits are phosphates, silicates, and carbonates.

kg/h)]. Fuels were switched between natural gas and No. 6 fuel oil until 1 month before failure, when oil was used exclusively. Original burners were replaced with larger burners.

Deposition was essentially due to excessive fire-side heat input. Overheating assisted by these deposits eventually caused failure. In addition, burner design and excessive steam production both contributed significantly to deposition and eventual overheating.