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REFINING
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DUAL CATALYST SYSTEMS

CORROSION CONTROL

HYDROPROCESSING CASES

Maximise utilisation of high-activity hydrotreating catalysts

Good practices to maximise product profit, extend run length, and improve reliability

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Imagine feeding the wrong crude blend into a refinery. The moment it hits the crude unit, there is no going back. Every downstream, unit will feel the consequences of the reduced capacity, unexpected constraints, efficiency loss, reliability incidents, and difficulty meeting product quality for the rest of the run.

The right catalyst defines what a unit can produce, and its utilisation decides how much of that promise is delivered. Today's refiners operate in a tighter window than ever: stricter product specs, more variable feeds, and longer run lengths between turnarounds. At the same time, heavier crudes and higher cracked stock content raise temperature requirements and accelerate catalyst deactivation. In some commercial units, the temperature increase requirement (TIR) has exceeded 1°C per month, a rate that can shorten cycles by several months.

Getting the most out of a high-activity hydrotreating catalyst is not about a single improvement. It takes discipline in several areas across the entire lifecycle. From the moment the catalyst is selected, every choice in handling, reactor design, loading, operation, optimisation, and monitoring influences whether that catalyst delivers its full potential or else falls short.

Several of the key areas to consider are summarised in the following discussions. Each topic has many associated good practices, which are beyond the scope of this article.

Catalyst selection

The first crucial step for the given refinery operation is catalyst selection. With many similar products available, a structured approach ensures the choice is based on both technical and economic factors. Several vendors should always be considered to find the best catalyst for the job and keep catalyst costs down by promoting competition, rather than getting locked into long-term contracts. Key criteria include:

- Relatively new catalyst performance compared to a well-known standard catalyst.
- Operating experience band and stability.
- Price and availability.
- Backup plans if performance falls short.
- Start-up and follow-up support.
- Hydrogen consumption.
- Start-of-run (SOR) and end-of-run (EOR) operating conditions.
- Yields and product properties.
- Any special handling or start-up procedures.
- Impact of a range of feeds (no single feed case).
- Exotherm potential on loss of recycled gas (impacts emergency procedures).
- Supplying existing vendor operational data for the preparation of a realistic proposal.

Performance guarantees should include correction factors. Even the same catalysts in similar units can behave differently because of variations in feed, reliability, and operations. Like crude blending, the choice must fit the specific unit, not just the market average. Choosing the right catalyst is much like tailoring a suit. The best material will only perform at its best if it is cut to fit the exact shape and requirements of the wearer. In the same way, a catalyst must be matched to the unique operating profile of its unit. It is then good to have a criteria checklist to compare the differences in the proposal.

Catalyst handling and storage

Once chosen, the catalyst must be protected until it is in the reactor. Obtaining samples ahead of time is important, as is checking labels on arrival. It is useful to perform rough strength tests for the associated larger inerts (non-catalytic bed materials used for support and flow distribution). Weak inerts can break down on loading, migrating, and increasing pressure drop.

Catalysts should be stored in rainproof and sunproof conditions upon receipt. Some catalysts are pre-doped with various hydrocarbons or sulphur compounds, which can decompose if heated but make start-up easier.

Always check immediately that the correct catalyst has been shipped and that inerts meet strength requirements. Protection up front prevents costly mistakes down the line.

Loading and unloading under nitrogen was common from the 1970s through the early 2000s. After several incidents in the mid-2000s, perhaps as operating experience lessened, some companies and regulators felt compelled to limit or prohibit reactor inert entry. While nitrogen-related incidents are rare, they are serious. Procedures have been further tightened to minimise incidents. Without nitrogen handling, reusable catalyst is often wet dumped, which increases catalyst cost, complicates reuse, and creates a wastewater production issue.

Reactor design

With the catalyst protected and stored correctly, attention turns to ensuring the reactor itself is ready to make the most of its potential. Several design parameters help obtain and maintain good catalyst performance, including dimensions, distribution, access, thermocouples, and catalyst dumping.

Bed diameter and height impact performance. Too large a diameter (to reduce pressure drop across the bed) and an excessively tall bed will lead to a higher level of maldistribution. Even a good distributor cannot completely fix the bed, and maldistribution worsens with bed height, especially with mixed-phase reactors. Hydrocracking bed heights are limited to control the heat rise in each bed. Hydrotreating beds can be much higher, but above about 6-7 metres, the maldistribution risk increases, regardless of distributor design.

Gas-liquid distributors and quench systems need proper installation and maintenance. Leak checks should be straightforward, even without full internal access. In one hydrocracker case study, properly maintained and upgraded internals increased effective catalyst utilisation by 29%.

Poor performance due to leakage has halved diesel unit activity. A good tray design should allow for easy leak testing and observation, especially if maldistribution is detected on the previous cycle. Maldistribution is better assessed by looking at the ratio of radial over axial 'delta T' (ΔT) rather than just radial delta, especially when the axial ΔT is not large (such as, access).

Access via side-entry manways in a multibed reactor is significantly easier for loading, monitoring, and maintenance. It is also much safer to work in emergencies, such as when exiting rapidly, when dealing with an injury. The side-entry manway flanges are not unevenly stressed, such as with the inlet and outlet, so leakage concerns are lower. It will add cost to the fabrication, which is why it is not so common in many companies.

Thermocouple location and thermowell design, if used, can impact bypassing if it is not done carefully. Thermowells penetrating the support trays are not preferred, and horizontal thermowells are considered much better. Flexible thermocouples are now more common to give significantly better bed coverage, but maintenance needs to be prepared for a higher frequency of repair need.

Skin temperatures, usually placed near the bottom of each bed, where maldistribution may be severe, are required for certain beds. This is particularly the case in hydrocrackers due to the exotherm risk, such as when recycle gas is lost or if there is severe flow maldistribution. A good practice at the bottom dump tube is to provide the option for a pressure gauge to be fitted. This allows the ΔP of the outlet collector to be checked.

Angled catalyst side dump nozzles can replace inter-bed dump tubes, which often contribute to maldistribution. Two dump tubes at each bed reduce the risk of localised plugging in one dump tube. Support grids are frequently based on fine grid screens rather than bars to keep inerts from migrating. However, they can be more easily damaged, so they should still have some inert ball grading below the catalyst.

Operations and maintenance checks before loading

Before loading, operations and maintenance checks should confirm that all reactor internals are installed and secured, including any tray gasketing or materials used to fill gaps. Tray level should be verified, and trays should be inspected for damage. If maldistribution is a concern or trays are newly installed, tray leak tests should be conducted.

Where the economics justify it, changeout time can often be reduced significantly through effective planning, clear procedures, good communication, and coordinated teamwork. Many other design considerations for preheat systems and recycle gas systems also contribute to maximising catalyst utilisation. Poor preparation will cause problems from the start, especially in relation to reduced activity, channelling, hot spots, and earlier colour problems.

Best practices for reactor loading

Reactor loading is critical to avoid maldistribution, pressure drop, or catalyst migration. Poor loading can quickly undermine the best design and catalyst choice. A good loading procedure avoids fines by limiting freefall when loading. Keep track of the catalyst amounts used and clearly mark bed heights. This information, along with the associated catalyst density checks, confirms an even loading. Bed grading in the guard bed is also important to protect against feed contaminants and migration. It is essential at the bottom of any bed to have a correct layer-to-layer particle size change to prevent catalyst migration.

There are several ways to transport catalyst to the reactor top, including one bag or two to three bags if the top platforms can handle the load. Hydraulic methods are also in use at some locations. Other key equipment to consider includes access to deliver catalysts to the site, dust extraction facilities, and procedures to minimise catalyst and inerts freefall.

Dense loading is now used on most units, except when putting in bed grading to open void fraction to manage fouling materials, remove metals, or if there are specific issues with highly viscous feeds. Several dense loading procedures are now used to achieve adequate packing, and dense loading should be considered unless special pressure drop constraints exist.

Dense loading reduces channelling, whereas sock loading often allows preferential unbalanced flow, as density is not uniform. Most of the different dense loading technologies work if there is a good technician and the site keeps in close contact. They will have different loading capacities and access needs, being able to load anything from approximately 8 to 20+ tonnes/hr.

Dense loading also allows more catalyst to be put in the reactor. If the density increase is less than 15% more than sock loaded then there is a problem with the dense loading process. A more densely packed bed will increase the pressure drop across the reactor bed, so dense loading is not practised in the guard bed. Some contractors also use fluidised continuous loading, though experience is lower and should be first tested in a less critical service.

While the various unloading options for spent catalyst (and the associated positives and negatives) are beyond the scope of this article, unloading options can involve dry dumping under nitrogen; wet dumping; passivation and air dumping; vacuum unloading with high and very low losses; use of high pressure jetting for catalyst balls and some fixed bed residue units; and occasionally use of small explosive charges.

Start-up procedures

Several factors can affect catalyst performance during pre-start-up and start-up. Care at this stage protects catalyst activity and prevents early-life damage.

Avoid using tankage feed unless it is well filtered. Storage tanks often introduce scale, sediment, and oxygen. Oxygen in cracked stocks can significantly increase polymer formation, leading to fouling and blocked flow paths.

After any required hydrotesting, clean the preheat system thoroughly and remove all water. A water slug can vapourise and wash debris into the reactor or quench zones, damaging trays.

Control heat-up rates to avoid thermal shock. Uneven heating can crack internals, damage catalyst structure, and cause maldistribution. This step may be limited by minimum pressurisation temperature constraints (MPT) if the reactor was specified to be too high. Designers do not always fully account for operations away from steady-state conditions.

Ensure catalyst passivation is adequate for hydrocracking catalyst, which is highly active at start-up. Temperature excursion has been seen when using liquid recycle to minimise slop, where organic nitrogen, which is a natural activity suppressor, is slowly removed through recycling in the reactor. Fully pre-activated catalysts eliminate the need for the sulphiding step and can cut start-up time. Even so, they still require controlled heating to protect the catalyst, reactor internals, and other mechanical equipment.

The quality of the procedures also impacts a successful start-up. It must have an adequate explanation and direction. If the intent and reason behind various steps are not understood, it will become difficult to manage any resulting unplanned events. There should be adequate checks and balances at the beginning and end of key steps, clearly outlining the state of the equipment. Any interactions with supply and product units should also be referenced within the procedure to make sure everything works in the correct sequences.

Added reliability is achieved with bar charts of the various steps so that key equipment conditions are known. There are marked-up flowsheets/sketches, so any different start-up routings are more easily understood than written instructions alone. For example, a procedure rarely relates all the equipment status on a block as the procedure progresses. This is very important to optimise time, avoid unexpected events, and better plan mechanical work.

To maximise catalyst utilisation, catalyst changeout time should be minimised. This requires the development of a good catalyst handling plan and create a good relationship with the catalyst handling and catalyst loading contractors.

Planning

Planning before shutdown is the most important task. A workshop for all stakeholders, well before the shutdown, should be called to discuss all the required actions to identify and apply the best ideas. This strategy has been successful at several sites, resulting not only in good catalyst performance but also much shorter shutdown times. KBC has seen this type of workshop process, with full stakeholder attendance, reduce catalyst changeout time by 30-50%. Good integration of processes with mechanical, inspection, and contractors are vital.

A set of key checklists for each phase of the shutdown is a good tool for benchmarking and identifying new opportunities, without omitting anything. Detailed checklists can be developed for all key steps in implementing the catalyst change and assigning a weighting to the various parameters. Some checklists contain up to 500 items. This also helps prioritise improvement areas and real roadblocks. Such a checklist can be broken down to include planning (the most important), safety and reliability procedures, catalyst handling, mechanical procedures around the reactor system, equipment design features, modifications and reactor design.

Benchmarking

Typically, benchmarking may compare total or individual time taken for different units. However, there are various other parameters to look at when performing a more realistic benchmarking, including catalyst volume, recycle gas rate capability, number of reactors, access, MPT restrictions, and even furnace capability, where start-up is often limited by furnace duty (when there is no heat rise in the reactor). Some of these factors, such as catalyst amount and recycle gas ratio, can be normalised to standard numbers to provide a more realistic benchmarking target for each step of the changeout.

Feed quality control

Feed quality is often the main factor that determines running length. Maximise direct feed wherever possible. Oxygen promotes free radical formation and polymer deposits, especially with cracked stocks. Mixing the feed with hydrogen early helps suppress polymer formation. Tankage feed is a source of scale, sediment, and oxygen. For example, some units processing part coker naphtha and tankage feed have fouling issues. Others, which have no intermediate tankage, have no fouling and must only worry about the silica. A fault tree-type approach to looking at feed quality issues is good. **Figure 1** shows a first-level fault tree for reviewing feed quality issues. Lower-level trees can exist for developing the more likely problem areas.

Filtration: Focus filtration on streams that have particulates resistance to upstream separation, such as coker streams. Measurement of solids in the streams will determine the need for filtering other streams. Limiting the feeds using the filters improves their effectiveness.

Fractionation: Control fractionation in the upstream fractionators to manage the feed endpoint, and for the heavier feed units, the level of metal contamination. The feed tail contains all the hard sulphur, so poor fractionation can significantly impact the weighted average bed temperature

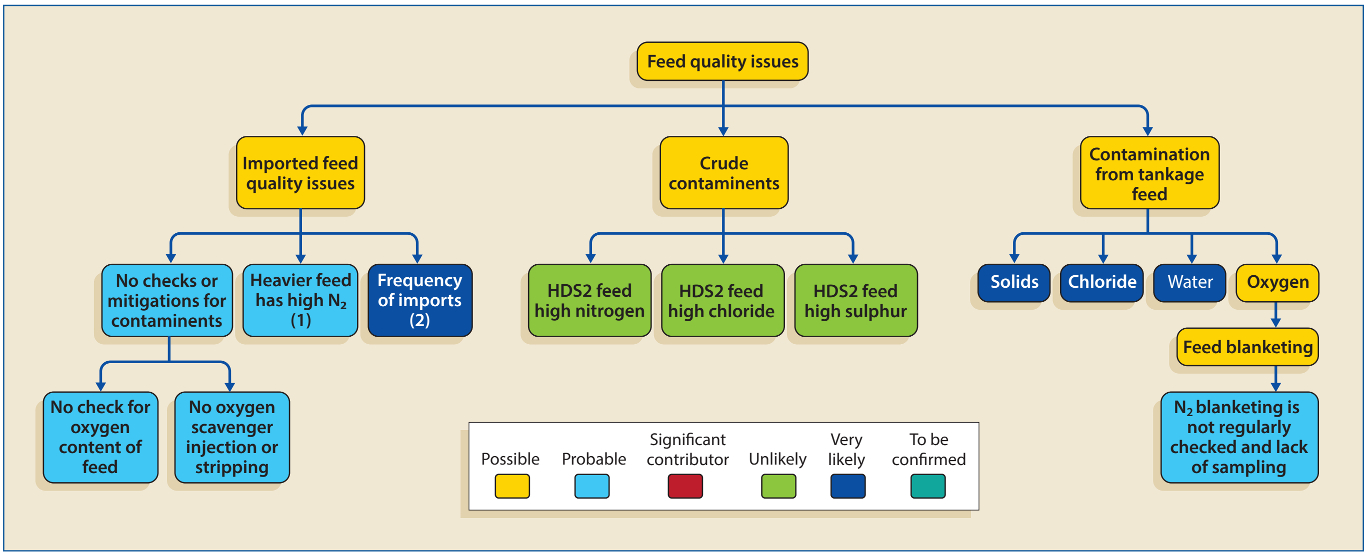

Figure 1 Feed contaminant source fault tree – top level

(WABT) requirement. When moving to a 10 ppm sulphur operation in diesel units, the better units switch from ASTM D86 to gas chromatography (GC) distillation to track fractionation.

Contaminants control: Contaminants can come from several sources. Slop processing on the crude unit is another unpredicted source of contaminants, such as chemicals, cracked stock, and oxygenates. Crudes can contain arsenic, organic chlorides, and other chemicals. Crudes from shale oils and fracking are notorious for having varying levels of contamination.

The key is that with a new feed, the correct feed analyses are done. There have been several cases of unexpected naphtha hydrotreater deactivation due to arsenic, as staff members rarely check naphtha for metals. Deactivation due to normal feed coking is usually zero, and contamination/fouling are causes of poor performance for these low severity-units, even at very low H_2 pp. Stable, clean feed to the catalyst is the foundation for predictable and efficient operation, as well as optimum cycle length.

Emergency and restart procedures

A good reaction to emergencies will preserve catalyst performance. One common mistake is trying to keep the unit online for too long. Procedures should be well understood and easy to access. They should include actions that, in severe situations such as fire, require certain instrumentation to be in place to remove the feed, fire source, isolation cooling, and pressure reduction.

Cooling should not rely on gas quench alone for control of exotherms. The heat source needs to be removed, and the system frequently cooled, even if it is by feed. In the case of fire, hydrocarbon sources should be isolated. The key, then, is cooling and depressurisation.

Controlled depressurisation, even before any emergency trip, is key to reducing the exotherm rate of change, maintaining equipment integrity, and creating inbuilt cooling in mixed-phase systems as the liquid vapourises. Controlled depressurisation, which can be slowed or halted, should be a primary tool for reactor protection.

Restart procedures are also important. Sometimes the intention is to restart as quickly as possible. However, this can cause more damage due to thermal stresses and create new shutdown situations. The frequency of shutdowns and thermal cycling should be built into equipment inspection frequency or even the need for hot bolting, as bolts relax.

Corrosion control

Corrosion is a particular concern in areas where water or salts can be present, such as reactor effluent air coolers (REAC). Report API 932B 2019 provides great guidance on REAC issues, which can significantly impact the unit and, thus, catalyst utilisation. REAC systems are susceptible to ammonium bisulphide corrosion. The API report recommends alloy selection, expected corrosion rates, water wash equipment requirements, and corrosion monitoring programmes to mitigate failures.

More difficult are chloride-related issues. Under-deposit corrosion from chloride salts, which is more difficult to detect and predict, is best addressed by much better mixing,

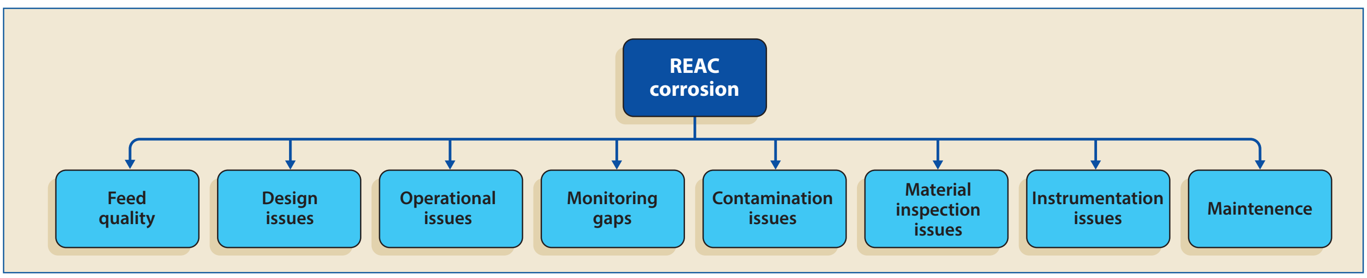

Figure 2 REAC corrosion top-level fault tree

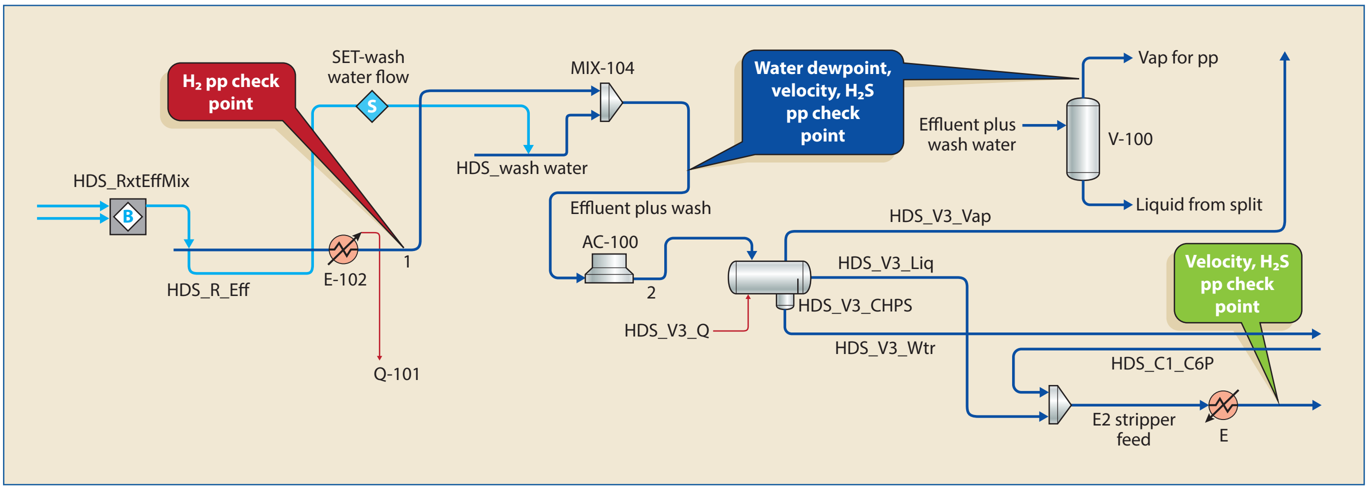

Figure 3 Example of potential fouling and corrosion mitigation solutions

an area not well addressed in many REAC corrosion mitigation documents. Without good mixing, water washes or chemical injection are not very effective.

With equipment process models, such as Petro-SIM, OLI, and other tools, all the parameters contributing to salt problems can be estimated. A key action will include keeping chlorides out of the system, as these are contaminants. **Figure 2** identifies areas to look at just for REAC corrosion mitigation opportunities. **Figure 3** shows some typical solutions that might be identified.

Monitoring and process conditions

Catalyst performance depends on more than steady-state operation. It requires ongoing monitoring of process, mechanical, and corrosion parameters, as well as the impact of unplanned events for equipment and catalyst. For example, the number of upsets, such as thermal cycle/shutdowns, can be linked to inspection requirements or even earlier hot bolting of flanges. This involved the integration of key performance indicator (KPIs) with integrity operating windows (IOWs). API RP 584 – Integrity Operating Windows (IOWs) gives guidance on IOW development for equipment.

The key is to integrate these IOWs with process KPI monitoring to create a more powerful tool. It is essential to include parameters that will identify impending short- and long-term problems, as well as target KPIs. This can include identification of changing corrosion rates, valve positions, fractionation loss, furnace operation, machinery efficiencies and exchanger fouling, as well as changes in deactivation.

Predictive modelling is now a great asset; digital twin models can further improve reliability and optimisation. Some operations have cut unplanned outages by integrating IOW and KPI monitoring and optimisation using digital twin models, such as those based on Petro-SIM. This is now advancing to AI-overseen applications, which should have a built-in knowledge base to manage any data analysis system.

Guidance correlations based solely on data analysis/self-learning have sometimes been completely wrong, as certain knowledge information was not accounted for. For example, in some units, deactivation from cracked stock was overestimated based on feed type data and deactivation. However, in reality, the perceived catalyst deactivation was due to fouling and maldistribution at the top of the bed, and most of the activity was fully recovered just by skimming the bed, reducing O_2 in feed.

Process conditions optimisation

Many parameters can be looked at to maximise catalyst utilisation within the operating envelopes, some of which are often overlooked. A few examples include:

- Feed quality control, including fractionation control, cut point control, and routing the best feed to the best unit, such as easier feed to lower H_2S partial pressure units.
- H_2 purity in recycle gas impacts performance and cycle length significantly, especially if below 95%. Even 1-2% makes a measurable difference. H_2 purity can be increased with more make/purge/use of amine scrubbers. Lower drum temperatures depending on the cost of H_2, if available.
- Furnace constraints can be mitigated with a change in quench targets, reducing preheat fouling by minimising tankage feed, drop-in recycle gas rates (if spare activity exists).
- Better analysis of deactivation and catalyst conditions.
- Hydraulic constraints can be overcome by running spare pumps in parallel. A more general practice now is to run all machinery to maximise capacity where pump curves permit.

Summary

Selecting the right high-activity catalyst is the first step in maximising its utilisation, especially now that harder feeds are processed and product quality is becoming more rigorous. Many of the areas discussed, if not addressed, can result in the credit for a higher activity catalyst being completely wiped out. Thus, for maximum catalyst utilisation, a multifaceted sustainment programme is required to maintain performance and maximise catalyst credits. In some actual cases where every constraint has been rigorously challenged, even a 'humble' diesel hydrotreater resulted in millions of dollars of additional revenue.

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