THE COLD-CRUCIBLE MELTER: A KEY TECHNOLOGY FOR THE DOE CLEANUP EFFORT

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ABSTRACT

The vitrification of high-level waste is the internationally recognized standard to minimize the impact to the environment resulting from waste disposal as well as to minimize the volume of conditioned waste to be disposed of.

COGEMA has been vitrifying high-level waste industrially for over 20 years and is currently operating three commercial vitrification lines based on a hot metal crucible technology, with outstanding records of safety, reliability and product quality.

To further increase the performance of vitrification facilities CEA, COGEMA and SGN have been developing the cold crucible melter technology since the beginning of the 1980s. This type of melter is characterized by a virtually unlimited equipment service life and a great flexibility in dealing with various types of waste. Its compact modular design enables significant cost savings on facility capital investment.

In order to demonstrate the CCM capabilities to efficiently process US DOE waste, a specific demonstration program has been set up and performed on the pilot facilities existing in France. Tests have been performed with Idaho and Hanford surrogate wastes. The results achieved for Hanford-type waste are presented hereafter.

INTRODUCTION

COGEMA, in collaboration with the CEA, has accumulated over 20 years of experience in industrial High-Level Liquid Waste vitrification. From the start of AVM in 1978, the design of COGEMA's vitrification plants (AVM, R7, and T7) has continuously improved through innovation and incorporation of operating experience. The presently operating facilities display high records of availability, safety and product quality: COGEMA facilities have produced more than 10,000 high-level glass canisters so far, representing more than 4,000 metric tons of glass and 3.5 billion Curies.

In order to extend the field of application of vitrification, the CEA and COGEMA have developed since the beginning of the 1980's a new melter, the CCM, which is much more resistant to corrosion than any other type of crucible and allows melting at temperatures never reached until now in industrial nuclear applications. From the origin, this melter has been specifically developed for nuclear applications, in compliance with the major design and maintenance principles successfully implemented in the presently operating COGEMA facilities. The CCM melter is small and easily maintainable, which allows implementing the technology in compact, low-cost facilities. The melter also incorporates features very favorable to the processing of glasses subject to solids crystallization and/or settling: possibility of mechanical stirring, high temperature, short residence time, efficient and reliable pouring device. The possibility to reach high temperatures opens the way to processing very refractory matrices and to increase the waste loadings, thus reducing the final wasteform volume. High temperatures also improve the melting rates.

This combination of very favorable characteristics - adaptation to operation in industrial nuclear environments, ease of maintenance, resistance to corrosion, possibility to melt at high temperatures – makes the CCM particularly suitable to provide new and efficient answers to some of the very demanding DOE cleanup challenges, such as in Hanford or Idaho.

In order to illustrate the interest of the CCM technology for USDOE waste, COGEMA and CEA have undertaken a proof-of-principle program on several surrogates, involving laboratory and pilot testing. Moreover, a cost/benefit analysis has been performed to assess the potential benefits of applying the CCM technology in an optimized HLW for the WTP at Hanford. The present paper describes the program related to Hanford-type wastes.

CCM DEVELOPMENT AND IMPLEMENTATION

CCM development

After the early selection of borosilicate glass as a preferred matrix, the continuous two-step process involving a rotary calciner and metallic hot crucible, developed since the 60s, has become the core of the industrial process since 1978. One major outbreak has been the implementation of mechanical stirring in 1996, which allows the routine incorporation of 3 wt% noble metals in the glass without any settling or pouring problems. In more than 20 years, this technology has demonstrated the advantages of using modular, small size equipment in terms of operability, remotability, maintenance and volume of secondary solid waste. The buildings required to house this small equipment can also be optimized to a reasonable size, thus minimizing the cost of investment or of future D&D. This technology has been able to fulfill all the needs in France until now and the facilities are still in excellent conditions for continued operation. The major drawbacks of this technology are the fact that the metallic crucible, although it is small and easy to change, and although its lifetime has been considerably improved (over 5000 hours), is subject to corrosion by the melt and the fact that melting temperature is limited to about 1150°C to preserve the integrity of this metallic melter.

In the 80's, in order to extend the field of application of vitrification, the CEA and COGEMA have initiated the development of a new melter: the CCM, essentially to improve the melter life-time by making it corrosion-proof, and to overcome the traditional temperature limits, thus allowing the processing of corrosive melts or of new matrices with higher waste loadings.

In the CCM concept, the glass "self-heats" by the Joule effect created by currents directly induced into the melt from external high frequency inductors. Because heat is not transmitted by conduction, the melter crucible can be cooled (hence the name "cold crucible"). This causes a thin layer of vitrified material to coat the walls, protecting them from corrosion. Since the heat is produced directly into the melt, high operating temperatures can be reached without any impact on the melter itself. We have experience today in melting and pouring a wide variety of molten salts, glasses, glass-ceramics and ceramic materials (including R7T7 glass melted at 1150°C, basalt melted over 1500°C, Synroc melted at 1600°C, or asbestos melted at 1800°C).

Pilot facilities supporting the CCM technology

Several test platforms have been built in the Marcoule pilot facilities since the 1980's in order to develop the Cold Crucible Melter Technology. These programs were initially focused on the treatment of HLW solutions from light water reactor fuel, producing the simulated R7/T7 glass.

The oldest platform is a stand-alone CCM pilot, which can be fed with simulated calcine and glass frit. The 550-mm diameter stainless steel melter can also be liquid fed. This platform, equipped with a 300 kW generator, has cumulated more than 5,000 hours of operation over a 15-year period. Approximately 50 metric tons of simulated HLW glasses were produced. Since the beginning of the CCM programs, most of the process demonstrations have been performed on this platform with solid and liquid feed.

The second platform is a full-scale mock-up of the R7/T7 vitrification process that can be equipped with a hot crucible melter or a 650-mm diameter CCM (with a 300 kW generator). In either case, the melter can be coupled to a calciner and fed with simulated calcine and glass frit. This platform is currently used to qualify the CCM process as it will be implemented in the R7 facility.

A third platform called EREBUS is dedicated to the more recent applications. It is equipped with a smaller, 160 kW generator able to operate at frequencies ranging from 200 to 500 kHz. It can be operated with melters of various diameters up to 1,000 mm. The selection of the diameter will depend on the type of test to be performed, while accounting for the limited available power. The feeding systems allow simultaneous controlled feeding of solids (frit, powders) and liquids (surrogate solutions, sludges). The off-gas system is composed of a condenser, an acid recombining/washing column before the extraction device.

An independent platform is also used for development of the incineration / vitrification process with a cold crucible melter. This process is well suited for the immobilization of intermediate or high level organic waste such as the ion exchange resins produced by Nuclear Power Plants. The organic matter is fed to the melter and is burned on the surface of the glass melt. The residual inorganic compounds are directly incorporated into the vitreous phase. The stainless steel CCM used on this platform has a diameter of 300 mm and is powered by a 240 kW generator. In order to finalize this development, a pilot industrial facility (equipped with a 550-mm crucible) has been built in collaboration with KEPCO/NETEC at Taejon in Korea (1).

Commercial applications of the CCM technology

COGEMA is already providing the CCM technology to international customers for nuclear and non-nuclear applications. For example, the CCM technology has been in operation for non-nuclear applications since 1995 to produce high added value glasses or enamels, with two melters. Because of the cold glass protection, glasses or enamels can be melted at high temperature with no pollution from the materials of the wall as in traditional glass melters. It is also possible to switch glass compositions in less than 8 hours since glass does not adhere to the cooled walls. In 1999, 500 tons of industrial glass of varying compositions have been produced with a single 1,200-mm diameter CCM.

This technology will be deployed at La Hague, in one existing vitrification line, to process specific corrosive, high viscosity material in the near future. For this application, the advantage of high temperature has been fully used by raising the target processing temperature from 1150°C to around 1350°C, thus allowing the selection of a new matrix resulting in a decrease of the overall glass volume by a factor of 3. The process and its ancillary technologies (pouring valve, instrumentation,…) have been qualified on the corresponding full-scale platform at Marcoule.

A CCM coupled with a calciner has been proposed for the Hanford TWRS-P Phase IA HLW studies (2). A large demonstration program, including the production of about 3t of surrogate glass on a pilot, provided confidence in the process and pointed to some possible advantages of further extending the range of conditions tested. More specifically, it was found that the technology displayed a potential for significant waste loading increases, thus reducing the volume of HLW glass to be disposed of.

This technology is also being supplied to foreign customers, with varying setups:

- CCM with direct liquid feeding to process legacy HLW in Italy
- CCM with direct liquid or solid (resin) feeding for simulated reactor waste in Korea (1).

ADVANTAGES OF THE CCM FOR THE VITRIFICATION OF US-DOE WASTE

Several sites in the US are planning to treat and immobilize large volumes of high-level waste stored in tanks and silos. The nature and composition of this waste is very variable, with a large number of challenges for the glassmaker.

Hanford High-Level Waste

At Hanford the High-Level Waste held in the tanks originates from several chemical separation processes and some tanks contain very high levels of elements known to limit the waste loading into the glass: chromium, zirconium, aluminum, phosphorus, fluoride…

The use of the CCM at high temperature would be of great use for instance to increase the amount of zirconium or aluminum in HLW glass, since these elements considerably increase glass viscosity. The tolerance of the CCM to crystal-forming elements is favorable to an increase in chromium content. This feature is very interesting since chromium is traditionally limited to very low contents in glass, especially with flat-bottom melters or melters that cannot easily remove settled crystal sludges. It has been recognized that chromium might be one of the elements determining the amount of High-Level Waste glass produced at Hanford. (3).

The resistance of the CCM to corrosive melts is a unique opportunity to process industrially high-phosphate waste into a borosilicate glass or another type of matrix if necessary: phosphate-rich melts are known to quickly attack refractories and electrodes in traditional LFCMs, leading to premature failures.

More generally, the use of a CCM would bring considerable flexibility towards waste composition and, thus, towards the retrieval sequence of waste from the various tank farms. It would also allow minimize the overall volume of High-Level Waste Glass produced: a reduction of High-Level Waste glass volume by 10 % would result in savings of around 2 billion dollars.

In the end, the compact, modular design of the melter allows a drastic reduction in size for a facility using this technology, when compared to a LFCM, as described in chapter 6. The consequence is a lower cost for both investment and D&D.

Hanford Low-Level Waste Vitrification

A significant issue at Hanford is the size of the melters required for processing Low Activity Waste at a rate compatible with the required overall plant capacity. The use of a small number of large LFCMs to fulfill this task leads to some uncertainties related to the design and construction, size and weight of equipment, procedures for maintenance and melter exchange, personnel exposure, volume and activity level of solid secondary waste that must be disposed of. The use of multiple, smaller CCMs in an adapted setting might help solve some of these issues.

Idaho

At INEEL, studies are under way to determine the path forward for immobilizing first the liquid sodium-bearing waste and, later, to dispose of the calcine stored in several bin-sets. Here again, the CCM could provide attractive solutions:

- The sodium-bearing waste could be directly vitrified in a liquid-fed CCM-based facility. This one-step operation would allow optimizing cost and delay.
- The calcine holds large amounts of either alumina or zirconium and calcium fluoride. These components could be a challenge for a traditional LFCM-based technology and would lead to large amounts of glass. The recommended approach for this situation would be to use a CCM operated at high-temperature to make glass-ceramics with high or very high (up to 60%) waste loadings.

In order to support the above statements, COGEMA and CEA have undertaken selected testing on surrogates representing typical US-DOE wastes. The next chapter describes the results obtained for Hanford wastes.

HANFORD WASTE TESTING

Tests have been performed on both LAW and HLW surrogates:

- The LAW surrogate composition was directly derived from the concentrated DSSF composition that had been tested during the vendor tests of 1994-1995 (4). The sodium concentration was set at 10N.
- The HLW surrogate compositions tested were derived from those already tested during phase IA (2): they represented NCAW (AZ101 and AZ102 tanks) and high-heat (C106 tank) wastes.

Hanford LAW surrogate

The LAW solutions are very rich in sodium and thus lead to glasses with specific physical properties.

The first part of the testing program consisted in validating the existing models and adapting the various platform parameters to this new type of glass. For this adaptation, a generic CEA high-sodium glass composition was used.

A second part of the testing program was aimed at assessing the major parameters governing the physics and chemistry of vitrification for this specific feed.

The DSSF surrogate was tested, together with the same generic high-sodium glass composition as above, in a small laboratory induction-heated crucible (Φ 130 mm) in a hood. The testing consisted in varying several operating parameters:

- Form and size of the glass-formers
- Feeding method for glass-formers
- Effect of other chemicals,
- Effect of temperature

These tests allowed evaluating the general behavior of the system: reactivity, foaming tendency, behavior and quality of the cold-cap, …The effect of temperature was found to be essential for both capacity and ease of operation.

The third part of the testing program involved larger scale demonstrations on the EREBUS pilot fit with a mechanical stirrer

A first series of tests was run to confirm that it was feasible to feed the CCM with a liquid LAW surrogate at this concentration, producing the same glass as above and using a generic CEA frit. The capacity reached in these conditions was around 60 kg of glass/h/m². For this test, the glass temperature was close to 1050°C at 2 cm below the surface. A consistent cold-cap, essentially composed of glass foam, was present, hampering heat exchanges between the glass and the feed.

In a second series of tests, the temperature was raised to 1300°C. The processing capacity then reached 100 kg of glass/h/m² (2.4 t/d/m²) in continuous feeding, which met the objective of the test and was generally far better than the results published for the vendor tests (5) or the contractual objective set for the WTP. During the test, the cold cap behavior improved considerably, it melted very easily into the glass, was very stable, without any foaming.

Conclusion

This preliminary testing provides encouraging results with respect to capacity and ease of operation, stressing once again the advantage of high-temperature operation. Some additional optimization pathways have been identified, such as the optimization of a glass formulation specifically adapted to this LAW solution, or the optimization of glass-formers and of their feeding method.

Hanford HLW surrogates

During phase IA, feeding of the CCM was performed through a calciner and gave very satisfactory results.

A program similar to that for LAW surrogates was started to evaluate direct feeding of HLW surrogates into the CCM. The surrogates used were directly derived from those used during phase IA, simulating NCAW (AZ-101 and AZ-102) and high-heat (C-106) sludges. The baseline glasses used were also those already designed during phase IA, since a good knowledge had been gained and these glasses were compliant with all the contractual requirements.

The feeding method was tested in the small hood melter

Some parameters tested included:

- Effect of the feed chemistry (acidic or alkaline)
- Form and size of the glass-formers
- Feeding method for the glass formers
- Effect of feed concentration
- Study of chemical additions, if required

The tests performed with both "AZ Blend" and "C-106" surrogates gave satisfactory results and pointed out that it was possible to reach adequate throughputs without foaming or melt instability. The glass temperature was around 1300 or 1400°C.

Pilot testing was then performed on the same platform as above (EREBUS) with a surrogate derived from the phase IA "C106" composition by subtracting minor and toxic elements and by substituting all alkalis by sodium and all rare earth elements by lanthanum. The fabrication recipe is directly derived from that developed by PNNL (5). The feed was quite dilute (around 100 g of oxides per liter). The frit was the same frit used during phase IA demonstrations

The waste loading into the glass was fixed at about 44 % to duplicate the glass that had been designed during phase IA, which corresponded to about 0.23 kg of glass per liter of feed. No attempt of waste loading optimization was performed at that stage; previous studies performed during phase IA had shown that, with the given waste composition, a waste loading of about 52 % could be reached. The feed rate in that case was about 150 l/h/m² (surrogate only) and the glass throughput was around 35 kg/h/m² (0.84 t/d/m²). No foaming or instability was observed. This capacity, with a dilute feed, is twice the initial design base value of 0.4 t/d/m² (17 kg/h/m²) for the HLW facility in the WTP. It was expected that, if more concentrated, the feed would allow much higher throughputs.

Indeed, for another test performed with a more concentrated (228 g oxide/liter), C106-type acidic solution, the maximum feed rate became 125 l/h/m² and the corresponding glass throughput was around 65 kg/h/m² (1.56 t/d/m²). For this test, the glass production rate was of 0.52 kg of glass/liter of feed.

For a concentrated, "AZ Blend"-type acidic solution, with a waste loading of about 31 % into the glass, the maximum feed rate was about 142 l/h/m² and the glass throughput reached 92 kg/h/m² (> 2.2 t/d/m²). The glass production rate was of 0.63 kg of glass/liter of feed.

These results show that the CCM technology is able to easily process Hanford HLW-type waste at throughputs compatible with the WTP industrial requirements. These results also emphasize that a considerable potential exists to enhance melter capacity, by adjusting, for instance, the concentration of the feed.

Study of waste loading increase

The present baseline formulations are quite satisfactory for pilot testing. However, since it had been seen during phase IA work that the use of the CCM would help increase the waste loadings for numerous waste types, some work has been started to test this suggestion with the "AZ-Blend" composition which is known to be limited by the liquidus temperature. The baseline waste loadings for phase IA was around 31 or 32% for this waste type. Some property/composition models derived from those used during phase IA (2) have been run to test higher waste loadings with the same waste and the same frit, but considering higher melting temperatures. While viscosity seems to level off with increasing waste loading, the liquidus temperature (temperature above which no crystal is present in the melt) continues to increase.

For a waste loading of 40 %, the liquidus temperature would be around 1170°C while the durability of the glass would remain acceptable. This glass could be melted around 1300°C. Such an increase in waste loading would reduce the volume of glass by about 25% when compared to the baseline value derived from the contractual requirements of phase IA.

A further increase in waste loading to 43% would further increase the liquidus (around 1220°C) and would bring the glass very close to the domain where nepheline (detrimental to glass durability) would form. Changing the composition of the frit does not lead to significant improvement A waste loading of 43% thus seems to be, for this specific waste composition, a fixed limit corresponding to glass quality requirements. The use of high temperatures in this case allows effectively reaching waste loadings close enough to this limit and thus minimizing the volume of glass to the lowest possible value.

Glasses for waste loadings of 38 % and 40% have been prepared by melting and refining for 3 hours at 1300°C at the crucible scale. They are in the course of being characterized. The following properties have been or will be determined:

- Leach testing in progress: Soxhlet, 7-day PCT, 56-day PCT, on quenched and heat-treated glasses
- SEM-EDS characterization for quenched and heat-treated samples. The heat-treatment approximates a CCC (Canister Centerline Cooling)-type curve. Quenched glasses are homogeneous with small silver grains. Heat-treated glasses include the same silver grains together with dendritic crystals, 50 micron-long and 2 or 3 micron-thick, enriched in iron and nickel oxides, which confirms the tendency to form "spinels" for these glasses. The amount of crystals is slightly higher for the more concentrated glass.
- Viscosity: for both glasses, the viscosities range from around 50 dPa.s at 1300°C to less than 115 dPa.s at 1200°C, which confirms the feasibility of melting these glasses at 1300°C.

Conclusion

These preliminary tests have demonstrated the possibility of liquid-feeding the CCM with specific throughputs easily compatible with industrial requirements and similar to or higher than those obtained in the new generation of LFCMs in comparable conditions. High-temperature melting has been demonstrated and has shown its advantages with regard to throughput and ease of operation. Some paths for improvement have been identified, related to chemical pretreatment and concentration of the feed, glass formulation, feeding method.

The potential of increasing waste loadings with increased melting temperature has been demonstrated for a specific High-Level Waste composition.

OUTLINE OF A HYPOTHETICAL FACILITY FOR HANFORD HLW VITRIFICATION

In order to demonstrate the cost benefit associated with the implementation of the Cold Crucible Melter in a setting making use of COGEMA's proven practices for design and operation, an optimized HLW plant has been designed for the Hanford case. The main drivers for this optimization study were:

- to decrease significantly the size of the HLW building by implementing a CCM and applying COGEMA's standards
- to reduce the risk by using the best proven technologies
- to draw on COGEMA's experience in designing and operating HLW vitrification facilities

This optimized design incorporates many proven COGEMA technologies among which:

- The COGEMA Cold Crucible Melter (CCM) technology to replace the GTS Duratek LFCM. The compact, modular design of the melter allows to drastically decrease the size of the building. All in-cell handling equipment can be downsized accordingly, with modules weighing less than 1 or 2 MT.
- the La Hague off-gas treatment system in operation at La Hague since 22 years
- COGEMA's in-cell recyclable metal filters that enable the elimination of the filter cave
- COGEMA's TIG welding system which simplifies canister welding
- COGEMA's high pressure water and sand blasting system for canister decontamination

The result of this optimization is a 65% reduction in HLW vitrification building footprint (as illustrated on figure 1 by the comparison between the current baseline and the optimized building) and a capital cost reduction of about $ 128 M.

Beside the capital cost reduction, $ 2.4 Billions could be saved on the life cycle cost as a result of the waste loading increase (possible thanks to the higher temperature that can be reached in the CCM) which impacts the final glass volume and by considerably reducing the need for melter exchange / disposal.

It also has to be pointed out that the inherent design features of the CCM eliminate many of the technical risks that are inherent to the LFCM (molten silver penetration in the grain boundaries, ceramic lining corrosion by sulfate and chlorides, noble metals behavior, complexity of melter exchange and internal decontamination operations, …).

All these optimizations reduce technical risk and provide cost savings by reducing HLW floor space requirements, eliminating ceramic melter construction and spent ceramic melter storage buildings, improving process reliability through use of proven design and operations techniques, and integrating process system design with proven maintenance philosophies.

CONCLUSION

The Cold-Crucible Melter developed by CEA and COGEMA is a technology that combines a very original and promising solution to overcome the traditional limits of glass melting in a nuclear environment with the application of experience-based design and operation principles. The resulting equipment is easy to operate and maintain, flexible, of a manageable size, and able to process an unprecedented range of materials. Its implementation in a HLW facility for Hanford-type wastes would lead to considerable life-cycle cost reductions.

Preliminary testing with several Hanford waste-types have confirmed interesting performances in terms of capacity (similar to or better than the values published for LFCMs and fully compatible with industrial objectives in the US), flexibility, and extension of the allowable composition domain. Liquid feeding has been demonstrated with this type of waste. Mechanical stirring and the possibility to reach high temperatures not only provide higher capacities and the possibility to process new matrices, but also allow reconsidering the operating philosophy, lessening the foaming and cold-cap control issues. Similar testing is now under way for Idaho-type surrogates (sodium-bearing waste and calcines).

A fully equipped testing platform of semi-industrial capacity is under construction at Marcoule, with design capacities of 50 kg of glass/h for typical HLW-type liquid feeding and 200 kg of glass/h for solid feed. This platform will include a CCM and numerous ancillaries, such as feed tanks with the corresponding feeding pumps, several possible trains of off-gas treatment (dry or wet)…, making it a powerful demonstration tool that could be used for a large range of surrogates, including US-types.

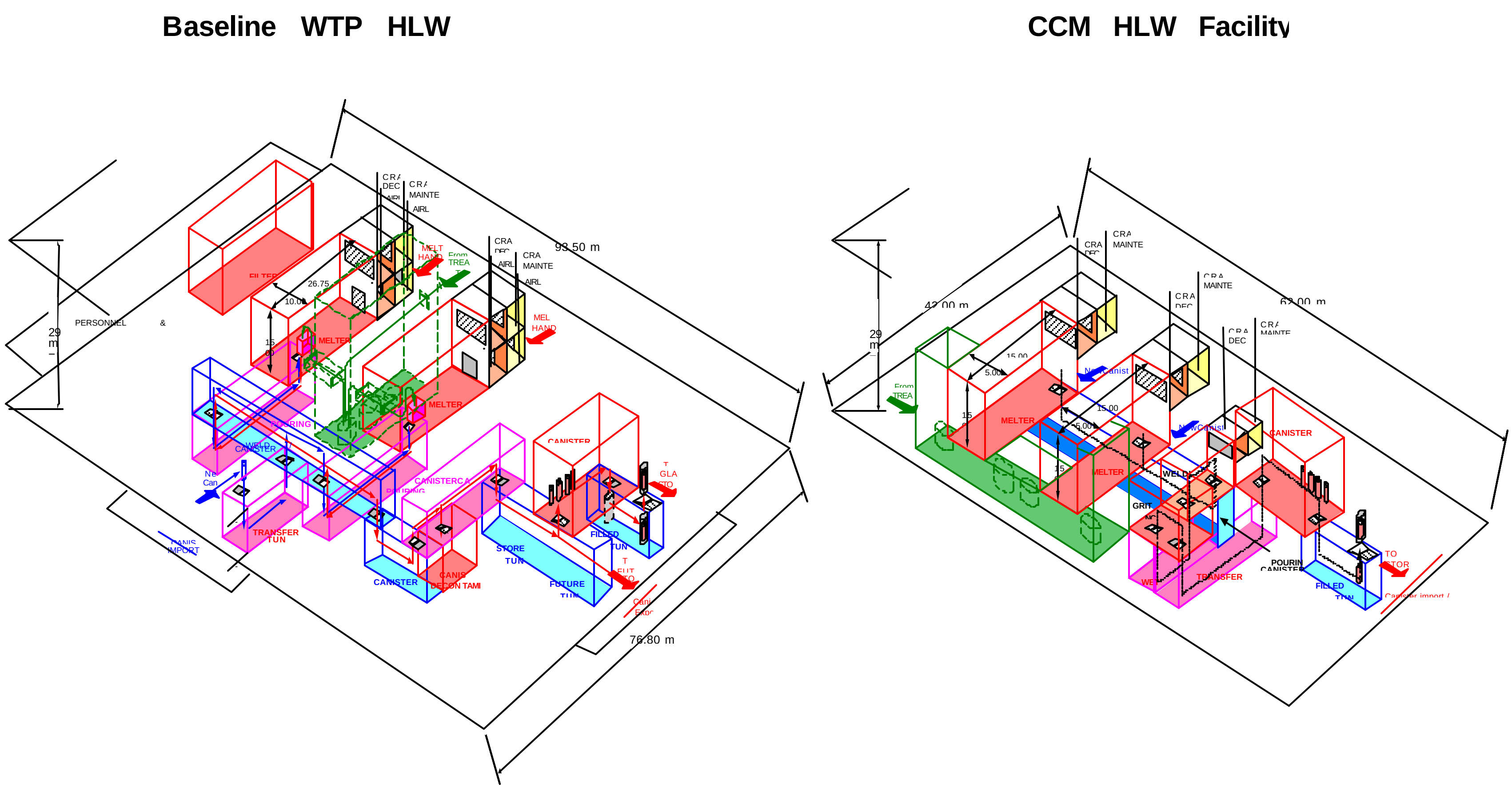

Fig. 1. comparison of facility layouts

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