

Recycling Used Engine Coolant; What Every Recycler Needs to Know

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INTRODUCTION

Approximately 2 billion pounds of concentrated antifreeze is produced in North America each year. About 80 percent of this is sold to refill leaking cooling systems¹; an estimated 7 percent is used for factory fill and 13 percent for coolant change-out. The amount of coolant changed-out is available for recycling or discharged to the sanitary sewer (See Figure 1). An overview of the composition and use of antifreeze (engine coolant) will be presented as well as a brief functional examination of the heavy-duty cooling system. A review and analysis of small and large scale commercially available antifreeze recycling methods will be presented.

Glycol based products have been used for many years to lower the freeze temperature and raise the boiling point of engine coolant. The glycol additive package provides cooling system corrosion protection. The majority of antifreezes in use today are based on ethylene glycol (EG), but propylene glycol (PG) products are becoming more common. EG products are less expensive than PG products, although PG products are less toxic. Engine-related applications of PG are usually found when environmental concerns have disallowed the use of the more common, EG products.

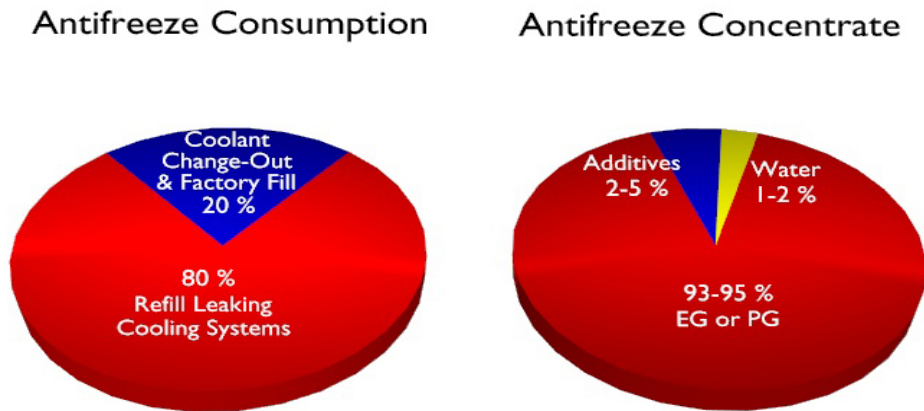


Figure 1

THE COOLING SYSTEM

Regardless of glycol type, engine coolant serves three main functions in a vehicle. These functions are heat transfer, freeze/boil-over and corrosion protection. Water is an excellent conductor of heat, but glycols are not as efficient, and so as a result, as the concentration of glycol increases, the heat transfer coefficient of the mixture decreases. To allow optimum heat transfer, modern engines are designed to run with a glycol/water blend of between 40/60 to 60/40 percent by volume, and so maintaining a fluid within the design parameters is important. Use of full strength antifreeze is not recommended because it leads to high engine operating temperatures and additive drop out that in turn causes plugging of cooling system passages and damaged water pump seals. The quality of water used to make-up an engine coolant is critical to ensure long cooling system and engine life, and deionized or distilled water is recommended.

Heavy-duty (HD) diesel engines require different coolant chemistry than gasoline engines to protect wet sleeve liners from pitting. To improve heat transfer and aid in serviceability, many HD engines incorporate wet sleeve liners. Under extreme stress of operation these liners vibrate. This vibration creates vapor bubbles that implode against the liners' outer surface. This action, called cavitation, can quickly eat a tiny hole in the liner allowing coolant to leak into the crankcase. Because of this problem, HD coolants must contain a special nitrite inhibitor, extra defoamer and buffers. These compounds are termed Supplemental Coolant Additives (SCA's).

USED ENGINE COOLANT

The recyclable components in used engine coolant are glycols and, for non-distillation techniques, water. Contaminants that either disqualify coolant or otherwise affect potential for economical recovery include engine gear and heating oil, gasoline, diesel, turbine fuel and kerosene, brake, transmission and hydraulic fluids, ammonia, and solvents. When the water concentration exceeds 70% recycling is usually not cost effective. Pollutant concentrations will vary in recycler feed stock and consistent operation cannot be maintained without reasonable quality control and an understanding of process limitations. Typical ranges of individual pollutants and undepleted additives in recycler feedstock are shown in Table 1. In the late 1960s and early 1970s toxicity and environmental concerns resulted in the elimination of chromate and arsenic from thermal transfer fluids². Used coolant from an individual vehicle can exceed these upper level concentrations by 5 times.

Table 1
Composition of Recycler Feed-Stock

<i>Parameter</i>	<i>Range¹</i>
Ethylene Glycol, %	35 – 58
Water, %	40 – 70
Conductivity, μS/cm	2800 – 5200
pH	7.8 – 9.8
CONTAMINANTS	
Oil, %	0.5 – 5
Total Organic Acids²	410 – 2600
Chloride	31 - 480
Sulfate	130 - 1750
Magnesium	2.1 - 8
Calcium	2.1 - 26
CORROSION PRODUCTS	
Aluminum	3 – 12
Copper	2.5 - 13
Iron	11 - 80
Lead	<2 - 17
Zinc	2.5 - 22
UNDEPLETED ADDITIVES	
Sodium Nitrite	85 - 1200
Sodium Nitrate	113 - 1350
Sodium Phosphate	780 - 2108
Sodium Tetraborate	210 - 1687
Sodium Molybdate	44 - 404
Sodium Silicate	24 - 200

¹ - Values in ppm unless noted otherwise

² - Glycol degradation products

RECYCLING ANTIFREEZE

Antifreeze recycling involves two separate processes 1) the combination of electro-physicochemical separations to consistently produce a glycol or glycol/water base stock of sufficient purity to reformulate to antifreeze and 2) corrosion control chemical reformulation to ensure its performance properties are indistinguishable from its virgin counterparts. Ingredients that ensure on or off-site success are good quality control and assurance, a well engineered and responsibly operated process, and OEM approved and proven reinhibition (glycol additive package) technology.

A number of separation techniques are used to recycle used engine coolant from the vehicular service industry. To achieve desirable results, a commercially successful recycling operation will use multi-stage processes as shown in Figure 2. Candidate treatment technologies, their function and side-streams generated are shown in Table 2. Removing a large portion of total dissolved solids (TDS) in a recycling process is key. Desalting technologies are essential unit operations required to produce an on-specification concentrate or pre-diluted recycled product and may include any one or combination of the following:

- Vacuum Distillation
- Membrane Separation
- Ion Exchange

PRETREATMENTS

Pretreatment of used engine coolant plays a vital role in the performance of downstream desalting systems. Gravity separation, chemical treatment and particle filtration are usually installed in front of desalting processes. Because of the high potential for organic fouling, effective pretreatment is more critical with membrane based systems and ion exchange than with distillation. Good pretreatment will improve recovery (flux rates) and, extend membrane life and cleaning intervals.

While particle filtration is the least expensive treatment for antifreeze, it is also the least effective method of producing on-specification engine coolant. This application involves pH adjustment, particle filtration, and addition of corrosion inhibitors. Antifreeze treated by this method is typically put back into the same car the fluid originally came from to avoid cross contamination between vehicles. After a period of time, a volume of antifreeze recycled in this manner builds up too many dissolved solids becoming very corrosive and will require change-out.

Most recycling techniques will use carbon adsorption as pretreatment or as a polish step to remove dissolved organics and color. Adsorption efficiency increases as contact time increases. Carbon adsorbers are typically operated at minimum flow rates of 3-5 gal/min-ft.² (for a 30 inch minimum bed depth). There are several choices among activated carbons. However, the most common selection is made from subbituminous, bituminous or lignite based coals.

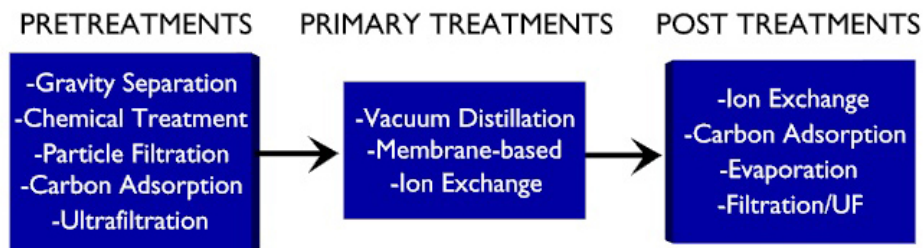


Figure 2

**Table 2
Candidate Treatment Technologies**

<i>Technology</i>	<i>Primary Function</i>	<i>Side-Streams</i>
GRAVITY SEPARATION		
Open Tank	Free Oil & Dirt Removal	Oils, Fuels, Sludge
Plate or Tube	“ “ “ “	“ “ “
Centrifuge	“ “ “ “	“ “ “
CHEMICAL TREATMENT		
Precipitation	Alter Solubility of Metals	Precipitants
Demulsification	Demulsify Soluble Oil	Oil
Coagulation/Flocculation	Conglomerate Particles	Sludge
PARTICLE FILTRATION		
Cartridge/Bag	Particle Separation,	Filters
Depth/Media	Filtration, Absorption	Media
MEMBRANE		
Ultrafiltration	Soluble Oil Removal	Reject, Cleaner
Nanofiltration	Multivalent Ion Removal	Wastewater &
Reverse Osmosis	Aqueous Salts	Membranes
ELECTRO-MEMBRANE		
Electrodialysis	Removal of Charged Ions	Brine, Membranes
Continuous Deionization	“ “ “ “	“ “
DISTILLATION	Water Evaporation, Salt-Out	Wastewater, Still Bottoms
POLISHING		
Carbon adsorption	Dissolved Organics, Color	Carbon
Ion Exchange	Removal of Trace Ions	Resins

VACUUM DISTILLATION

Vacuum distillation is an established method used at large fixed sites and if soundly designed and responsibly operated, can produce a concentrate glycol compliant with ASTM specifications. Small scale vacuum distillation processes are commercially available but are normally slow (1-3 gallons per hour) with low recoveries. Large fixed distilleries are built to different specifications and with dissimilar equipment than small scale units³. Fully equipped quality assurance laboratories are typically on-site at large distilleries to predict both product quality and plant operational problems. Vacuum distillation has the additional advantage of removing water, allowing for the production of concentrate antifreeze. Cost per installed capacity is highest for vacuum distillation compared to other primary treatments.

MEMBRANE SEPARATION TECHNIQUES

A number of membrane based systems may be used to pretreat or to desalt the preconditioned coolant. These may be categorized as either pressure or electro-driven. Pressure-driven membranes discriminate by particle size whereas electro-membrane methods discriminate by ionic charge.

PRESSURE-DRIVEN MEMBRANES

Ultrafiltration (UF) typically rejects organics over 1,000 molecular weight (MW) while passing ions and small organics and is typically combined with Nanofiltration (NF). UF can process oily, turbid used antifreeze to generate semitransparent permeate while experiencing minor irreversible membrane fouling. UF will not produce an engine coolant of sufficient purity to meet virgin specifications.

Nanofiltration (NF) is an option to provide removal effectiveness, in terms of molecule/ion size, that ranges between UF and reverse osmosis (RO), as shown in Figure 3. NF, a term coined by FilmTech in 1984 (now a division of Dow) employs a more porous membrane than true RO. NF is also referred to as membrane softening and is a pressure-driven semipermeable membrane process with a wide range of performance characteristics. NF does not retain/reject smaller, lesser-charged species like chloride and is usually unable to produce an engine coolant of sufficient purity to meet virgin specifications. Some NF membranes are similar to UF membranes in that these have an appropriate MW cutoff (MWCO) and so can be used to pass EG while retaining color, a portion of multivalent ions (hardness, etc.), and other contaminants. As a result, NF membranes will retain a portion of ions contributing to conductivity and generate permeate that is near water white (usually light yellow). However, because of scaling and fouling potential, NF membranes cannot treat used engine coolant as direct feed without pretreatment to remove the fouling components.

In reverse osmosis (RO), influent water is forced through a semipermeable membrane from a region of higher salt concentration to a more dilute region by applying a pressure, which is greater than osmotic pressure. Under normal osmotic pressure, water would move from the more dilute side to the more concentrated side. Left behind is concentrated brine, commonly referred to as reject. RO rejects most components other than water and operates at a pressure of 250-1000 psi. Membranes rejecting EG can be used to concentrate glycols for applications like airport deicing fluid run-off diluted with water. This is typically practical when the initial EG feed concentration is <6% and it is useful to concentrate the dilute EG to the maximum achievable concentration of 10-12% at an operating pressure of 1,000 psig.

In order to recycle vehicle antifreeze, which typically contains $\geq 30\%$ EG, membranes that can pass both EG and water are necessary. Thin-film composite polyamide membranes are typically reported as allowing both EG and water to pass through, with adequate rejection of salts and other contaminants. Like NF, RO will have scaling and fouling potential that has to be dealt with on a case-by-case basis. The primary problem with NF/RO pressure-based membranes is the presence of emulsified oils. Oils coat (foul) the surface of the membrane resulting in a drastic reduction in production rate. When fouling is noted, the system must be shut down and cleaned. These procedures are time consuming, use expensive detergents, generate wastewater and the downtime reduces productivity. In addition, multi-stage and multi-pass systems are typically necessary in order to achieve economical recoveries⁵⁻⁶.

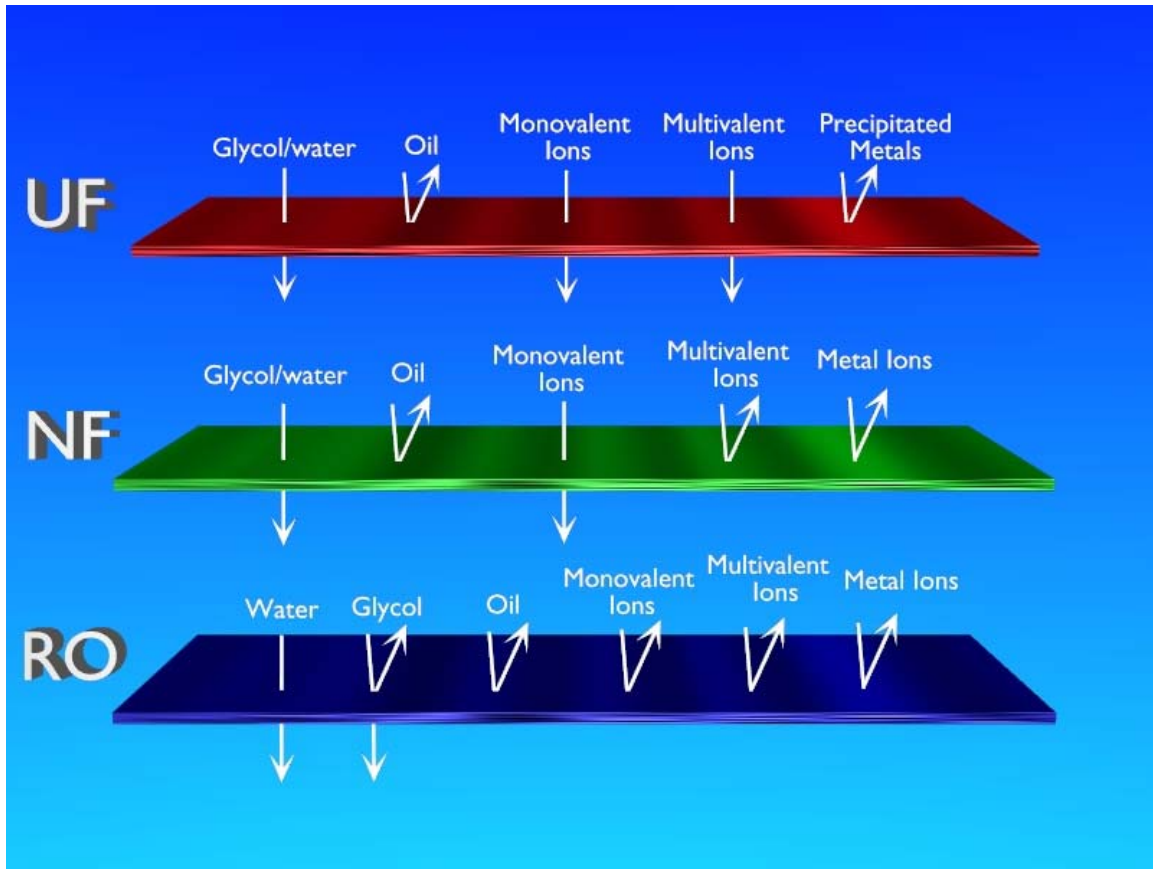


Figure 3

ION EXCHANGE (IE)

IE can produce a product compliant with virgin specifications. IE resins consist of spherical beads approximately 0.5-1.2 mm in diameter and are classified into cation and anion material. In an IE process, undesirable ions are removed from an aqueous stream and replaced with another ion. The cation resins contain functional sites capable of exchanging positive ions, and the anion resin contains functional sites capable of exchanging negative ions. Cost per installed capacity is lowest for ion exchange. However, due to the high concentration of ions in used engine coolant, expensive resins exhaust quickly exceeding the practical limits for its use in large fixed-site locations unless it is used as a polish step. An average processing cost (excluding labor, overhead and equipment amortization) for on-vehicle recycling is reported to be \$3.00/gallon⁶. Use of carbon in advance to adsorb organics is required to protect the resins from organic fouling, which renders the resins ineffective. The sequence of cation exchange followed by anion exchange resins is critical so as not to form insoluble metal hydroxides in the anion exchange column, which would restrict flow and quickly foul the system⁶.

ELECTRO-MEMBRANE

What makes electro-membrane processes, which include electrodialysis (ED), electrodeionization (EDI) or continuous deionization (CDI), unique and different from evaporative techniques and other membrane based processes is that they move dissolved minerals away from the glycol-water stream rather than the reverse, as illustrated in Figure 4. Because the quantity of minerals in the feed stream is far less than that of the fluid, this feature offers many practical advantages. In these processes, ions (ionized and ionizable species) are transported through a membrane from one compartment to another under the influence of an electrical potential. EDI is a relatively new process, which combines electrodialysis and ion-exchange by placing resin beads in the diluting compartments of an ED stack, continuously producing a desalted stream without chemical regeneration required by conventional ion exchange. EDI is usually used after RO or ED for polishing.

High Efficiency Electrodialysis (HEED™) is a new patents pending electrodialysis stack configuration developed by EET Corporation that incorporates dual or multiple side-by-side ion exchange membrane cells and an improved gasket design that results in greater separation efficiencies. The improved design bridges the gap of removal effectiveness between ED and EDI and is capable of removals down to low, sparingly conductive levels as shown in Table 3. HEED™ requires 40 percent less membrane area and is 70 percent more energy efficient than traditional ED stacks. Engine coolant recycled by HEED™ meets the virgin standard for pre-diluted engine coolant.

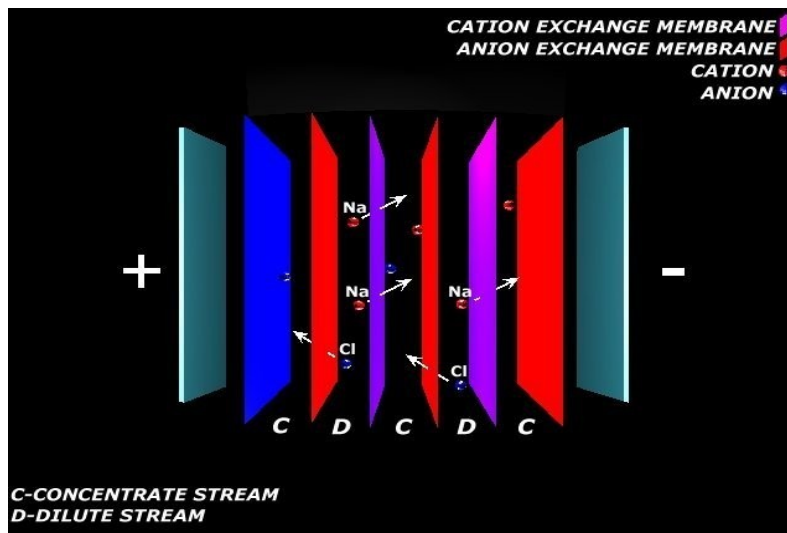


Figure 4

Table 3
Typical Glycol Desalting Performance
Using High Efficiency Electrodialysis (HEED™)

<i>PARAMETER</i>	<i>Used Engine Coolant</i>	<i>Conductivity 2000 (μS/cm)</i>	<i>Conductivity 1000 (μS/cm)</i>	<i>Conductivity 500 (μS/cm)</i>	<i>Conductivity 30 (μS/cm)</i>
Total Acids, ppm	1092	566	200	95	ND
Chloride, ppm	68	28	9	4	ND
Sodium Nitrite, ppm	2271	851	244	83	ND
Sodium Nitrate, ppm	1319	544	165	61	ND
Sodium Phosphate, ppm	1242	115	54	27	ND
Sulfate, ppm	228	107	40	17	ND
Sodium Molybdate, ppm	527	244	98	37	ND
Sodium Tetraborate, ppm	1587	807	650	511	21
Sodium Silicate, ppm	200	68	65	60	8
Aluminum, ppm	3	ND	ND	ND	ND
Copper, ppm	4	ND	ND	ND	ND
Iron, ppm	20	ND	ND	ND	ND
Lead, ppm	18	1	ND	ND	ND
Zinc, ppm	13	2	ND	ND	ND
Magnesium, ppm	8	1	ND	ND	ND
Calcium, ppm	26	7	2	ND	ND
pH	8.6	8.1	7.9	7.7	6.4

ND – Not Detected

SUMMARY

A number of methods are capable of producing recycled products to compare favorably with new (virgin) antifreeze/coolant formulated with the same inhibitor technology. What constituent limits and performance tests are acceptable for recycled antifreeze has caused considerable confusion with end users, recyclers and government agencies. ASTM, OEM, and various states have developed guidelines and regulations that govern the quality of recycled antifreeze. What is acceptable to one entity is likely in conflict with another. The best recycling approach is to conform to virgin requirements. Conformance to virgin glycol requirements reduces the “inferior-product” stigma associated with the reuse of antifreeze.

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